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(21) International Application Number: PCT/US97/16697 (22) International Filing Date: 22 September 1997 (22.09.97) (30) Priority Data: 9619921.1 24 September 1996 (24.09.96) GB 9622679.0 31 October 1996 (31.10.96) GB (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BROOKER, Alan, Thomas [GB/GB]; 41 Polwarth Road, Gosforth, Newcastle-upon-Tyne NE3 5NE (GB). MOSS, Michael, Alan, John [GB/GB]; 13 Painshawfield Road, Stocksfield, Northumberland NE43 7DZ (GB). FIGUEROA, Francisco, Ramon [VE/GB]; 35 Preston Wood, North Shields, Tyne & Wear NE30 3LT (GB). ASKEW, Stuart, Clive [GB/GB]; 17 Mayfair Road, West Jesmond, Newcastle-upon-Tyne NE2 3DN (GB). SORRIE, Graham, Alexander [GB/GB]; 14 Curlew Hill, Lancaster Park, Morpeth, Northumberland NE61 3SH (GB). HALL, Robin, Gibson [GB/GB]; 27 Blackfriars Court, Stowell St., Newcastle-upon-Tyne NE1 4XB (GB).		(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: DETERGENT COMPOSITIONS (57) Abstract <p>The present invention relates to granular detergent compositions or components thereof, which comprise a hydrophobic organic peroxyacid bleaching system, capable of providing a hydrophobic organic peroxyacid compound and one or more cationic compounds, which are cationic, (partially) quaternized ethoxylated (poly) amine compounds with clay-soil removal/anti-redeposition properties, for use in laundry and dish washing processes. Preferably, also a non-hydrophobic bleach system is present.</p>		

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Detergent Compositions

Technical Field

The present invention relates to granular detergent compositions or components thereof containing cationic compounds with particulate/clay-soil removal/anti-redeposition properties and a hydrophobic organic peroxyacid bleaching system for use in laundry and dish washing processes.

Background to the Invention

A particularly important property of a detergent composition is its ability to remove particulate type soils from a variety of fabrics during laundering. Perhaps the most important particulate soils are the clay-type soils. Clay soil particles generally comprise negatively charged layers of aluminosilicates and positively charged cations (e.g. calcium) which are positioned between and hold together the negatively charged layers.

A variety of models can be proposed for compounds which would have particulate/clay-soil removal properties. One model requires that the compound have two distinct characteristics. The first is the ability of the compound to adsorb onto the negatively charged layers of the clay particle. The second is the ability of the compound, once adsorbed, to push apart (swell) the negatively charged layers so that the clay particle loses its cohesive force and can be removed in the wash water.

In addition to clay soil removal, there is a need to keep the removed soil in suspension during the laundering (or dish washing) cycle. Soil which is removed

from the fabric and suspended in the wash water can redeposit on the surface of the fabric. This redeposited soil causes a dulling or "greying" effect which is especially noticeable on white fabrics. To minimise this problem, anti-redeposition agents can be included in the detergent composition.

For example EP-B-111 965 discloses the use in detergents of cationic compounds, which have both clay-soil removal and anti-redeposition properties.

US 4,659,802 and US 4,664,848 describe quaternized amines which have clay-soil removal and anti-redeposition properties and which can be used in combination with anionic surfactants.

A model proposed for the anti-redeposition action of the positively charged anti-redeposition compounds is as follows. Adsorption of the positively charged molecule on the surface of clay particles in the wash water gives the particles the dispersancy properties of the molecule. As more and more of these compounds adsorb onto the suspended clay soil particles, the latter become encased within a hydrophilic layer provided by the attached ethoxy units. As such the hydrophilically encased soil is prevented from redepositing on fabrics, in particular hydrophobic fabrics such as polyester, during the laundering or dish washing cycle.

Another component traditionally used in detergent is bleach, to remove bleachable stains or soils from the fabric.

A disadvantage of the use of most bleaches is that various other detergent components are bleach sensitive and that they can be oxidised by the bleach, whereby their original properties can be diminished. Thus, not all detergent components are bleach-compatible.

The Applicants have found that cationic, (partially) quaternized ethoxylated (poly) amines which have clay-soil removal/anti-redeposition properties, are fully compatible with bleaches formulated therewith.

It also has been found that the use in detergent compositions (or components thereof) of (oxygen-releasing) bleach in combination with fully quaternised ethoxylated (poly) amines provides a better improvement in cleaning or whiteness maintenance

than the use of (oxygen releasing) bleach in combination with partially quaternised ethoxylated (poly) amines. However, even the partially quaternised ethoxylated (poly) amines provide an improvement in cleaning or whiteness maintenance in combination with bleach.

Without wishing to be bound by theory, the bleach-compatibility of the cationic, quaternized ethoxylated (poly) amines can be explained as follows. The quaternization of the nitrogen groups of these molecules is believed to have a dual purpose. It provides a cationic charge on the molecule, improving adsorption onto clay particles either on the fabric surface or dispersed in wash water, and it removes the oxidisable lone pair on the nitrogen groups from attack by bleaching species, thus making the molecule stable in a bleach containing laundry detergents.

Recently developed bleach species are bleaching systems based on hydrophobic peroxyacids.

It has been found that one problem with hydrophobic bleaches is that despite their tendency to migrate to the hydrophobic stains or soils on the fabric surface, they do not necessarily interact fully with these. It has been found that the hydrophobic bleaches can be prevented from migration onto hydrophobic bleachable stains/soils by deposited clay-soil particulates on the fabric. Thereby, their bleaching performance can be diminished. This results in a lessening of the bleachable/ dingy soil cleaning performance of the hydrophobic bleach.

It also has been found that the removal of bleachable stains or soils on negatively charged fabric (such as fabric at high pH, cotton fabric or fabric surfaces containing negatively charged particles/ compounds, such as anionic surfactants) by hydrophobic bleaches is not always satisfactory. This is thought to be due to a lessened tendency of negatively charged hydrophobic bleaches to migrate to negatively charged fabric surfaces.

It has also been found that the removal of certain hydrophilic bleachable stains (such as beverage stains) by hydrophobic bleach is not always satisfactory, which is believed to be due to the limited interaction between the hydrophilic stains and hydrophobic bleach.

The Applicants have found that these problems can be ameliorated by the inclusion of one or more compounds which have clay-soil removal/anti-redeposition properties (as mentioned above) in a detergent composition, comprising a hydrophobic bleach. It has been found that in detergent compositions comprising both components the bleach efficacy of the hydrophobic organic peroxyacid bleaching system is enhanced. Furthermore it has been found that the bleach efficacy can also or further be enhanced by inclusion of non-hydrophobic bleaches in the bleach system. In both situations the overall cleaning performance of the detergent is improved.

The following mechanisms are believed to be responsible therefor. Firstly, it is believed that the interaction between the cationic compound and the anionic, hydrophobic (and also non-hydrophobic) bleach facilitates the migration and/ or interaction of the bleach to a negatively surface. Secondly, the interaction between the cationic compound and the (hydrophobic) bleach makes the bleach more hydrophilic, thus facilitating the migration or interaction of the bleach with hydrophilic, bleachable stains.

All documents cited in the present description are, in relevant part, incorporated herein by reference.

Summary of the invention

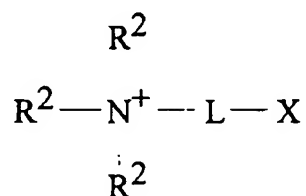
The present invention relates to granular detergent compositions or components thereof, which comprise a hydrophobic organic peroxyacid bleaching system, capable of providing a hydrophobic organic peroxyacid compound and one or more cationic compounds, which are cationic, (partially) quaternized ethoxylated (poly) amine compounds with particulate/ clay-soil removal / anti-redeposition properties.

In more detail, the present invention relates to granular detergent compositions or components thereof, which comprise

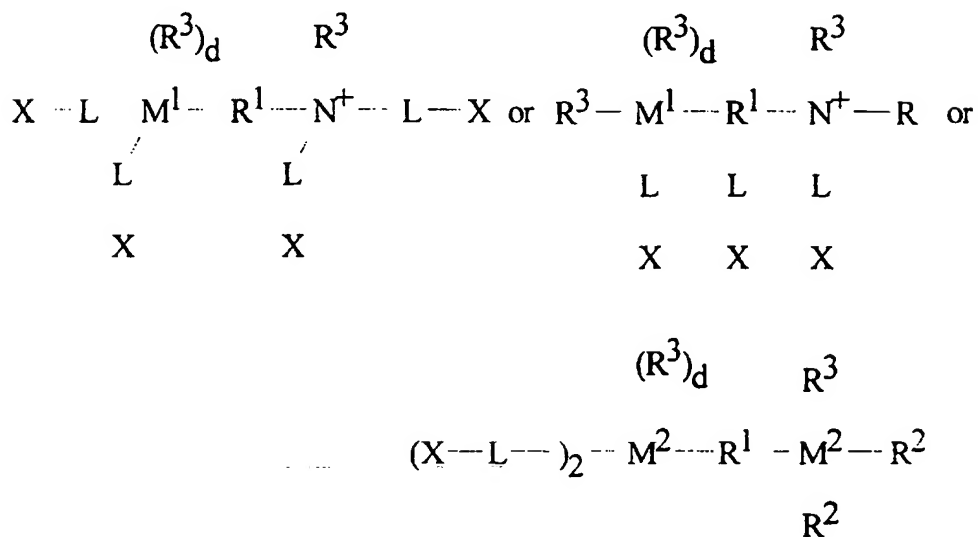
- (a) a hydrophobic organic peroxyacid bleaching system, capable of providing a hydrophobic organic peroxyacid compound; and

(b) a water-soluble cationic compound
having clay soil removal/anti-redeposition properties, which is
selected from the group consisting of:

1) ethoxylated cationic monoamines having the formula:

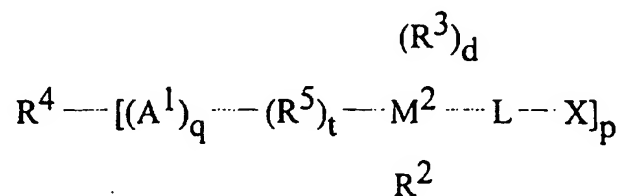


2) ethoxylated cationic diamines having the formula:

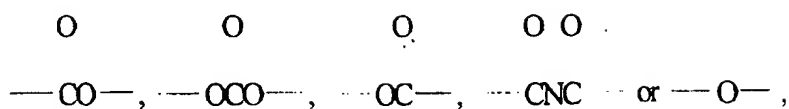
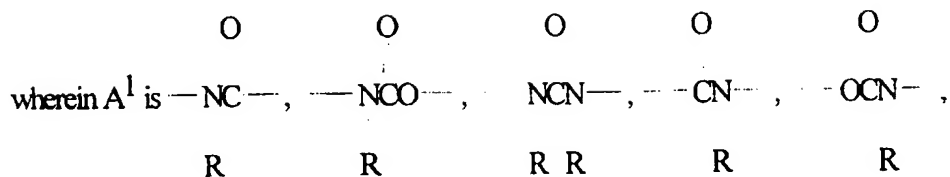


wherein M^1 is an N^+ or N group; each M^2 is an N^+ or N group, and at least one M^2 is an N^+ group;

3) ethoxylated cationic polyamines having the formula:



4) mixtures thereof;



R

R is H or C₁-C₄ alkyl or hydroxyalkyl, R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R² is C₁-C₄ alkyl or hydroxyalkyl, the moiety -L-X, or two R² together form the moiety -(CH₂)_r-A²-(CH₂)_s-, wherein A² is -O- or -CH₂-, r is 1 or 2, s is 1 or 2 and r + s is 3 or 4; each R³ is C₁-C₈ alkyl or hydroxyalkyl, benzyl, the moiety L-X, or two R³ or one R² and one R³ together form the moiety -(CH₂)_r-A²-(CH₂)_s-, R⁴ is a substituted C₃-C₁₂ alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl group having p substitution sites; R⁵ is C₁-C₁₂ alkenyl, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed; X is a nonionic group selected from the group consisting of H, C₁-C₄ alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof; L is a hydrophilic chain which contains the polyoxyalkylene moiety

-[(R⁶O)_m(CH₂CH₂O)_n]-; wherein R⁶ is C₃-C₄ alkylene or hydroxyalkylene and m and n are numbers such that the moiety

-(CH₂CH₂O)_n- comprises at least about 50% by weight of said polyoxyalkylene moiety; d is 1 when M² is N⁺ and is 0 when M² is N; n is at least about 16 for said cationic monoamines, is at least about 6 for said cationic diamines and is at least about 3 for said cationic polyamines; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1.

In a preferred aspect said hydrophobic organic peroxyacid bleaching system comprises (i) a hydrogen peroxide source and (ii) a hydrophobic organic peroxyacid bleach precursor compound.

In another preferred embodiment a non-hydrophobic bleaching system is present, preferably comprising (i) a hydrogen peroxide source and (ii) a non-hydrophobic bleach precursor compound.

Detailed description of the invention

An essential feature of the present invention is a water-soluble cationic compound which has particulate/ clay-soil removal/anti-redeposition properties and which is selected from the group consisting of cationic mono-di- and polyamines.

In detergent compositions, the water-soluble cationic compound is preferably present at a level of from 0.01% to 30%, more preferably from 0.1% to 15% , most preferably from 0.2% to 3.0% by weight of the detergent composition.

The ratio of the hydrophobic organic peroxyacid compound (provided by the hydrophobic organic peroxyacid bleaching) to the water-soluble cationic compound is preferably from 20:1 to 1:2, more preferably from 10:1 to 1:1, most preferably from 7:1 to 1:1.

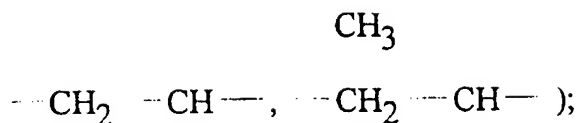
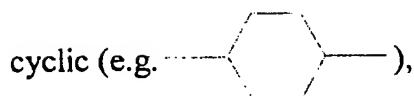
Cationic amines

The water-soluble cationic compounds of the present invention useful in the granular detergent compositions or components thereof in accord with the present invention include ethoxylated cationic monoamines, ethoxylated cationic diamines and ethoxylated cationic polyamines as previously defined.

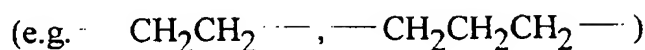
In the preceding formulas for the cationic amines, R^1 can be branched

(e.g.

8

C₃

or most preferably linear



alkylene, hydroxyalkylene, alkenylene, alkarylene or oxyalkylene. R¹ is preferably C₂-C₆ alkylene for the ethoxylated cationic diamines. Each R² is preferably methyl or the moiety -L-X; each R³ is preferably C₁-C₄ alkyl or hydroxyalkyl, and most preferably methyl.

The positive charge of the N⁺ groups is offset by the appropriate number of counter anions. Suitable counter anions include Cl⁻, Br⁻, SO₃⁻², PO₄⁻², MeOSO₃⁻ and the like. Particularly preferred counter anions are Cl⁻ and Br⁻.

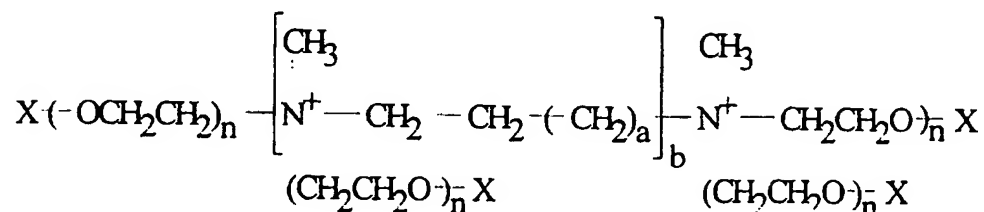
X can be a nonionic group selected from hydrogen (H), C₁-C₄ alkyl or hydroxyalkyl ester or ether groups, or mixtures thereof. Preferred esters or ethers are the acetate ester and methyl ether, respectively. The particularly preferred nonionic groups are H and the methyl ether.

In the preceding formulas, hydrophilic chain L usually consists entirely of the polyoxyalkylene moiety $\text{---}[(\text{R}^6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]\text{---}$. The moieties $\text{---}(\text{R}^6\text{O})_m\text{---}$ and $\text{---}(\text{CH}_2\text{CH}_2\text{O})_n\text{---}$ of the polyoxyalkylene moiety can be mixed together or preferably form blocks of $\text{---}(\text{R}^6\text{O})_m\text{---}$ and $\text{---}(\text{CH}_2\text{CH}_2\text{O})_n\text{---}$ moieties. R⁶ is preferably C₃H₆ (propylene); m is preferably from 0 to about 5 and is most preferably 0, i.e. the polyoxyalkylene moiety consists entirely of the moiety $\text{---}(\text{CH}_2\text{CH}_2\text{O})_n\text{---}$. The moiety $\text{---}(\text{CH}_2\text{CH}_2\text{O})_n\text{---}$ preferably

comprises at least about 85% by weight of the polyoxyalkylene moiety and most preferably 100% by weight (m is O).

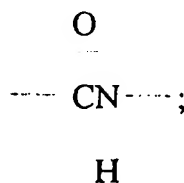
In the preceding formulas, M^1 and each M^2 are preferably an N^+ group for the cationic diamines and polyamines.

Preferred ethoxylated cationic monoamines and diamines have the formula:



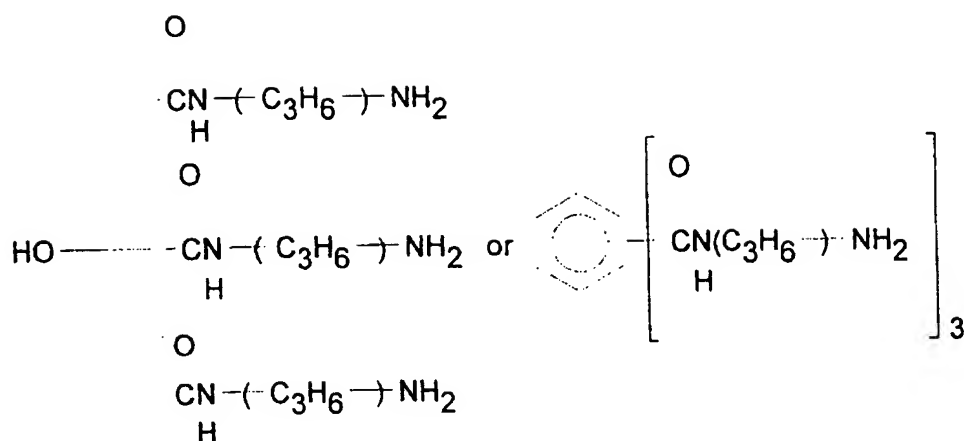
wherein X and n are defined as before, a is from 0 to 20, preferably 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0. For preferred cationic monoamines (b=0), n is preferably at least about 16, with a typical range of from about 20 to about 35. For preferred cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.

In the preceding formula for the ethoxylated cationic polyamines, R^4 (linear, branched, or cyclic) is preferably a substituted C_3 - C_6 alkyl, hydroxyalkyl or aryl group; A^1 is preferably

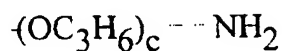
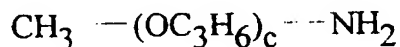
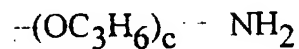


n is preferably at least about 12, with a typical range of from about 12 to about 42; p is preferably from 3 to 6. When R^4 is a substituted aryl or alkaryl group, q is preferably 1 and R^5 is preferably C_2 - C_3 alkylene. When R^4 is a substituted alkyl, hydroxyalkyl, or alkenyl group, and when q is 0, R^5 is preferably a C_2 - C_3 oxyalkylene moiety; when q is 1, R^5 is preferably C_2 - C_3 alkylene.

These ethoxylated cationic polyamines can be derived from polyamino amides such as:



These ethoxylated cationic polyamines can also be derived from polyaminopropyleneoxide derivatives such as:



wherein each c is a number from 2 to about 20.

Hydrophobic organic peroxyacid bleaching system

An essential feature of detergent compositions or components thereof in accord with the invention is a hydrophobic organic peroxyacid bleaching system, capable of providing a hydrophobic organic peroxyacid compound. By hydrophobic organic peroxyacid compound it is meant herein an organic peroxyacid whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre and

wherein said critical micelle concentration is measured in aqueous solution at 20°-50°C.

Preferably the hydrophobic organic peroxyacid bleaching system comprises a hydrogen peroxide source and a hydrophobic organic peroxyacid bleach precursor compound. The production of the hydrophobic organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. In an alternative preferred execution the hydrophobic organic peroxyacid bleaching system comprises a preformed hydrophobic organic peroxyacid, which is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and hydrophobic organic peroxyacid precursor in combination with a preformed hydrophobic organic peroxyacid are also envisaged.

Preferably, the hydrophobic organic peroxyacid contains at least 7 carbon atoms, more preferably at least 9 carbon atoms, most preferably at least 11 carbon atoms. In a preferred aspect the peroxyacid has an alkyl chain comprising at least 7 carbon atoms, more preferably at least 8 carbon atoms, most preferably at least 9 carbon atoms.

The ratio of the hydrophobic organic peroxyacid compound (provided by the hydrophobic organic peroxyacid bleaching) to the water-soluble cationic compound is preferably from 20:1 to 1:2, more preferably from 10:1 to 1:1, most preferably from 7:1 to 1:1.

Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the alkali metal, preferably sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however,

the preferred executions of such granular compositions utilise a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

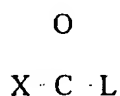
Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula $\text{NaBO}_2\text{H}_2\text{O}_2$ or the tetrahydrate $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$.

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid.

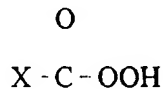
Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Peroxyacid bleach precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



For the purposes of the present invention X will thus contain at least 6 carbon atoms.

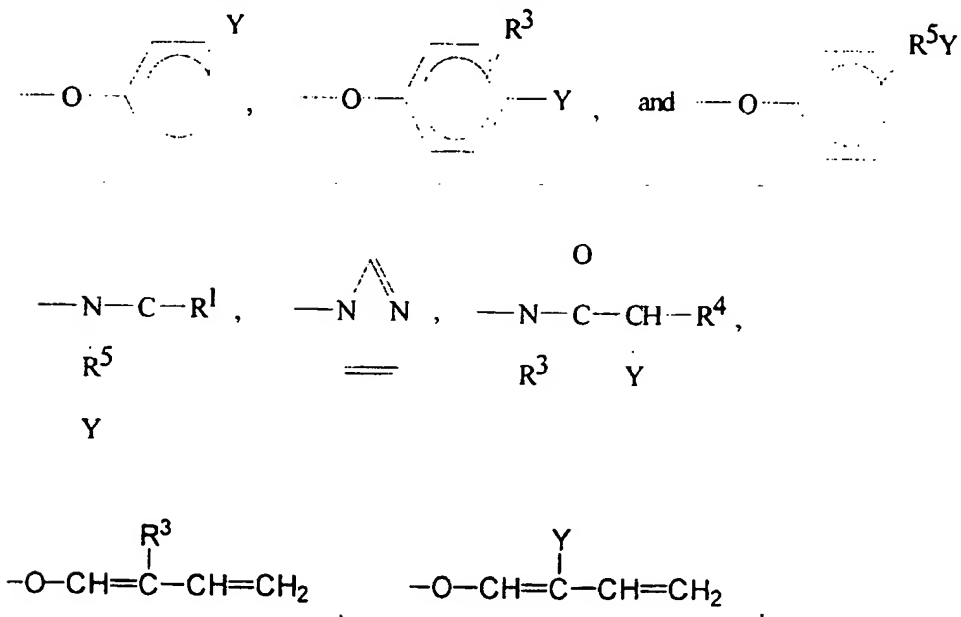
The hydrophobic peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.05% to 20% by weight, more preferably from 0.1% to 15% by weight, most preferably from 0.2% to 10% by weight of the detergent compositions.

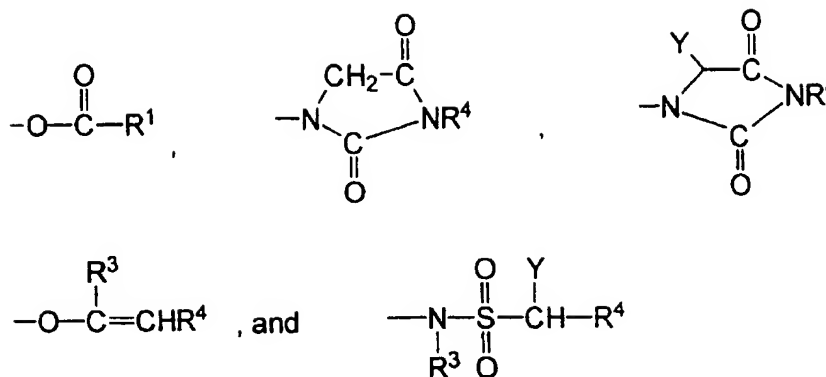
Suitable hydrophobic peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Leaving groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:



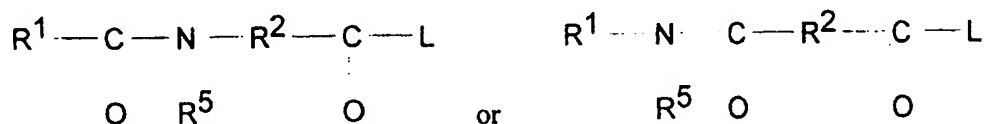


and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms. R^4 is H or R^3 , R^5 is an alkylene chain containing from 1 to 8 carbon atoms and Y is H or a solubilizing group. Any of R^1 , R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups

The preferred solubilizing groups are $-\text{SO}_3^- \text{M}^+$, $-\text{CO}_2^- \text{M}^+$, $-\text{SO}_4^- \text{M}^+$, $-\text{N}^+(\text{R}^3)_4 \text{X}^-$ and $\text{O}=\text{N}(\text{R}^3)_3$ and most preferably $-\text{SO}_3^- \text{M}^+$ and $-\text{CO}_2^- \text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Amide substituted alkyl peroxyacid precursors

Preferred peroxyacid precursors are amide substituted alkyl peroxyacid precursor compounds, including those of the following general formulae:



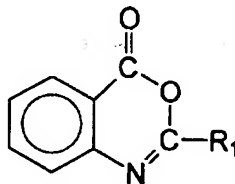
wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14

carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2 . R^2 can include alkyl, aryl, wherein said R^2 may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Preferred examples of bleach precursors of this type include amide substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzene- sulfonate, and the highly preferred (6-nonanamidocaproyl)oxy benzene sulfonate, and mixtures thereof as described in EP-A-0170386.

Benzoxazin organic peroxyacid precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:



wherein R_1 is an alkyl, alkaryl, aryl, or arylalkyl containing at least 5 carbon atoms.

Alkyl percarboxylic acid bleach precursors

Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred alkyl percarboxylic precursor compounds of the imide type

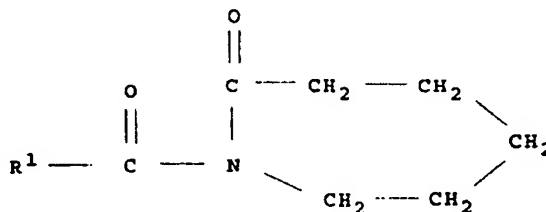
include the N-,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains at least 7 carbon atoms.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS) and sodium nonanoyloxybenzene sulfonate (NOBS).

N-acylated lactam precursors

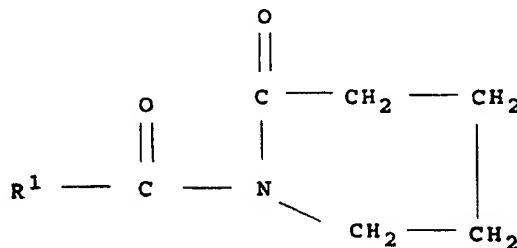
Still another class of hydrophobic bleach activators are the N-acylated precursor compounds of the lactam class disclosed generally in GB-A-955735. Preferred materials of this class comprise the caprolactams.

Suitable caprolactam bleach precursors are of the formula:



wherein R¹ is an alkyl, aryl, alkoxyaryl or alkaryl group containing from 6 to 12 carbon atoms. Preferred hydrophobic N-acyl caprolactam bleach precursor materials are selected from benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam and mixtures thereof. A most preferred is nonanoyl caprolactam.

Suitable valero lactams have the formula:



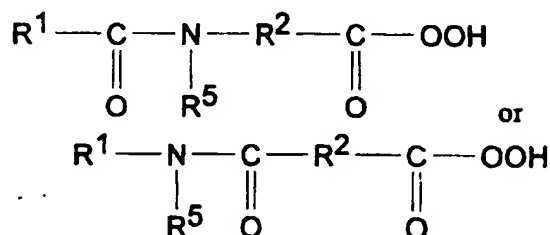
wherein R^1 is an alkyl, aryl, alkoxyaryl or alkaryl group containing from 6 to 12 carbon atoms. More preferably, R^1 is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

Mixtures of any of the peroxyacid bleach precursor, herein before described, may also be used.

Preformed organic peroxyacid

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed hydrophobic organic peroxyacid, typically at a level of from 0.05% to 20% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of hydrophobic organic peroxyacid compounds are the amide substituted compounds of the following general formulae:

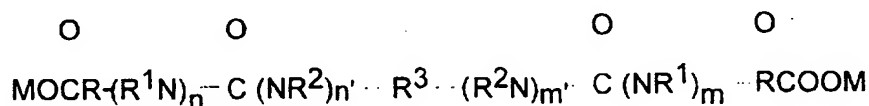


wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2 . R^2 can include alkyl, aryl, wherein said R^2 may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386. Suitable examples of this class of agents include (6-octylamino)-6-oxo-caproic acid,

(6-nonylamino)-6-oxo-caproic acid, (6-decylamino)-6-oxo-caproic acid, magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. 4,483,781, U.S. 4,634,551, EP 0,133,354, U.S. 4,412,934 and EP 0,170,386. A preferred hydrophobic preformed peroxyacid bleach compound for the purpose of the invention is monononylamido peroxycarboxylic acid.

Other suitable organic peroxyacids include diperoxyalkanedioc acids having more than 7 carbon atoms, such as diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid.

Other suitable organic peroxyacids include diamino peroxyacids, which are disclosed in WO 95/ 03275, with the following general formula:



wherein:

R is selected from the group consisting of C₁-C₁₂ alkylene, C₅-C₁₂ cycloalkylene, C₆-C₁₂ arylene and radical combinations thereof;

R¹ and R² are independently selected from the group consisting of H, C₁-C₁₆ alkyl and C₆-C₁₂ aryl radicals and a radical that can form a C₃-C₁₂ ring together with R³ and both nitrogens; R³ is selected from the group consisting of C₁-C₁₂ alkylene, C₅-C₁₂ cycloalkylene and C₆-C₁₂ arylene radicals; n and n' each are an integer chosen such that the sum thereof is 1; m and m' each are an integer chosen such that the sum thereof is 1; and

M is selected from the group consisting of H, alkali metal, alkaline earth metal, ammonium, alkanolammonium cations and radicals and combinations thereof.

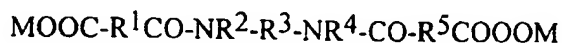
Other suitable organic peroxyacids are include the amido peroxyacids which are disclosed in WO 95/ 16673, with the following general structure:



in which X represents hydrogen or a compatible substituent, Ar is an aryl group, R represents $(CH_2)_n$ in which $n = 2$ or 3 , and Y and Z each represent independently a substituent selected from hydrogen or an alkyl or aryl or alkaryl group or an aryl group substituted by a compatible substituent provided that at least one of Y and Z is not hydrogen if $n = 3$. The substituent X on the benzene nucleus is preferably a hydrogen or a meta or para substituent, selected from the group comprising halogen, typically chlorine atom, or some other non-released non-interfering species such as an alkyl group, conveniently up to C6 for example a methyl, ethyl or propyl group. Alternatively, X can represent a second amido-percarboxylic acid substituent of formula:-



in which R, Y, Z and n are as defined above.



wherein R^1 is selected from the group consisting of C_1 - C_{12} alkylene, C_5 - C_{12} cycloalkylene, C_6 - C_{12} arylene and radical combinations thereof; R

Non-hydrophobic peroxyacid bleach precursor

Preferably a non-hydrophobic peroxyacid bleach precursor is present in the detergent compositions or components thereof. This can be any peroxyacid bleach precursor, not being a hydrophobic peroxyacid bleach precursor as defined above. Preferably the non-hydrophobic peroxyacid contains less than 7 carbon atoms, more preferably less than 5, most preferably 2.

Other peroxyacid bleach precursors are those, which can be a precursor for both hydrophobic and non-hydrophobic peroxyacids.

The non-hydrophobic peroxyacid bleach precursors are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the compositions.

The ratio of the non-hydrophobic peroxyacid bleach precursor to the cationic compound is preferably from 20:1 to 1:10, more preferably from 10:1 to 1:1, most preferably from 7:1 to 1:1.

Suitable peroxyacid bleach precursors typically contain one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Preferred non-hydrophobic peroxyacid bleach precursors are alkyl fatty peroxyacid bleach precursors, perbenzoic acid precursor, perbenzoic acid derivative precursors and cationic peroxyacid precursors.

Alkyl fatty peroxyacid bleach precursors

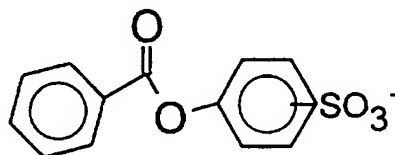
A highly preferred additional peroxyacid bleach precursor is an alkyl fatty peroxyacid bleach precursors. Alkyl fatty peroxyacid bleach precursors form alkyl fatty peroxyacids on perhydrolysis. Preferred precursors of this type give rise to peracetic acid on perhydrolysis.

Preferred alkyl fatty peroxyacid precursor compounds of the imide type include the N-,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

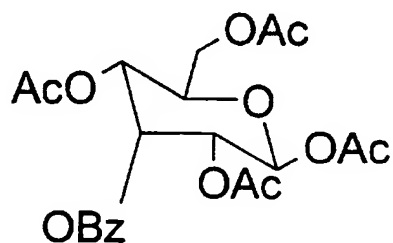
Perbenzoic acid precursor

Essentially any perbenzoic acid precursors are suitable herein, including those of the N-acylated lactam class, which are preferred.

Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, including for example benzoyl oxybenzene sulfonate:



Also suitable are the benzylation products of sorbitol, glucose, and all saccharides with benzoylating agents, including for example:

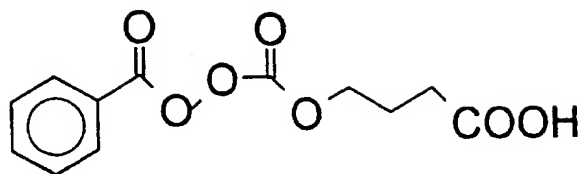


Ac = COCH₃; Bz = Benzoyl

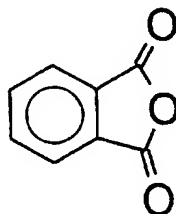
Preferred perbenzoic acid precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Preferred perbenzoic acid precursors include the benzoyl diacyl peroxides, the benzoyl tetraacyl peroxides, and the compound having the formula:

22



Phthalic anhydride is another suitable perbenzoic acid precursor compound herein:



Perbenzoic acid derivative precursors

Suitable perbenzoic acid derivative precursors include any of the herein disclosed perbenzoic precursors in which the perbenzoic group is substituted by essentially any functional group including alkyl groups.

Cationic peroxyacid precursors

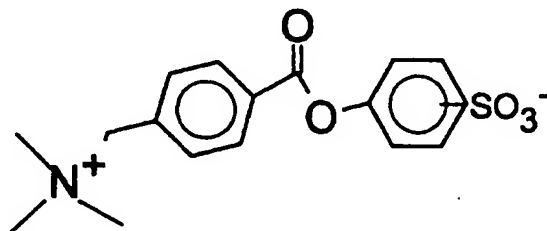
Cationic peroxyacid precursor compounds are also suitable herein. Typically such cationic peroxyacid precursors are formed by substituting the peroxyacid part with an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group.

Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

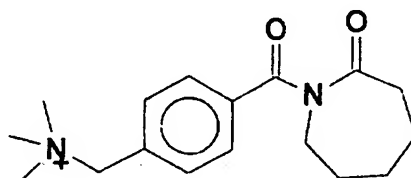
Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides.

A preferred cationically substituted benzoyl oxybenzene sulfonate is the 4-(trimethyl ammonium) methyl derivative of benzoyl oxybenzene sulfonate:



A preferred cationically substituted alkyl oxybenzene sulfonate is the methyl ammonium derivative of 2,3,3-tri-methyl hexanoyloxybenzene sulfonate.

Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams, particularly trimethyl ammonium methylene benzoyl caprolactam:



Another preferred cationic peroxyacid precursor is 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride.

Cationic polymers

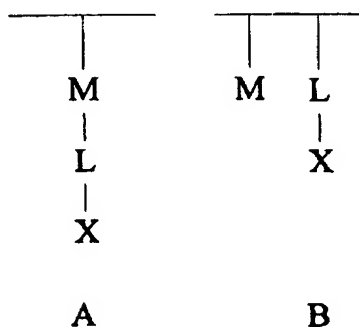
The detergent composition or component thereof can comprise additional polymeric cationic ethoxylated amine compounds with particulate/ clay-soil removal/ anti-redeposition, selected from the group consisting of water-soluble cationic polymers. These polymers comprise a polymer backbone, at least 2M groups and at least one L-

X group, wherein M is a cationic group attached to or integral with the backbone; X is a nonionic group selected from the group consisting of H, C₁-C₄ alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof; and L is a hydrophilic chain connecting groups M and X or connecting X to the polymer backbone.

The polymeric cationic ethoxylated amine compounds can be present in detergent compositions at a level of from 0.01% to 30%, more preferably from 0.1% to 15%, most preferably from 0.2% to 3% by weight of the detergent composition.

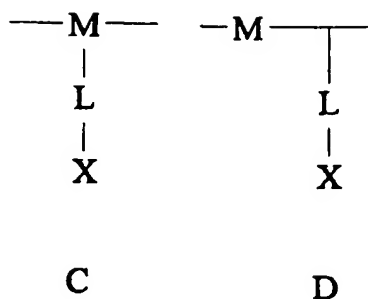
As used herein, the term "polymer backbone" refers to the polymeric moiety to which groups M and L-X are attached or are integral with. Included within this term are oligomer backbones (2 to 4 units), and true polymer backbones (5 or more units).

As used herein, the term "attached to" means that the group is pendent from the polymer backbone, examples of such attachment being represented by the following general structures A and B:



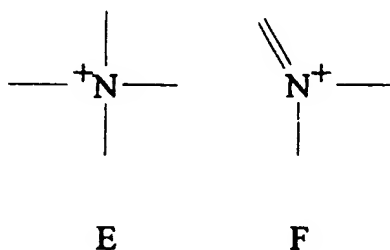
As used herein, the term "integral with" means that the group forms part of the polymer backbone, examples of which are represented by the following general structures C and D:

25



Any polymer backbone can be used as long as the cationic polymer formed is water-soluble and has clay soil removal/anti-redeposition properties. Suitable polymer backbones can be derived from the polyurethanes, the polyesters, the polyethers, the polyamides, the polyimides and the like, the polyacrylates, the polyacrylamides, the polyvinylethers, the polyethylenes, the polypropylenes and like polyalkylenes, the polystyrenes and like polyalkarylenes, the polyalkyleneamines, the polyalkyleneimines, the polyvinylamines, the polyalylamines, the polydiallylamines, the polyvinylpyridines, the polyaminotriazoles, polyvinyl alcohol, the aminopolyureylenes, and mixtures thereof.

M can be any compatible cationic group which comprises an N^+ (quarternary), positively charged center. The quarternary positively charged center can be represented by the following general structures E and F:



Particularly preferred M groups are those containing a quarternary center represented by general structure E. The cationic group is preferably positioned close to or integral with the polymer backbone.

The positive charge of the N^+ centres is offset by the appropriate number of counter anions. Suitable counter anions include Cl^- , Br^- , SO_3^{2-} , SO_4^{2-} , PO_4^{2-} , MeOSO_3^- and the like. Particularly preferred counter anions are Cl^- and Br^- .

X can be a nonionic group selected from hydrogen (H), C₁-C₄ alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof. The preferred ester or ether groups are the acetate ester and methyl ether, respectively; The particularly preferred nonionic groups are H and the methyl ether.

The cationic polymers suitable for use in granular detergent compositions or components thereof in accord with the present inventions normally have a ratio of cationic groups M to nonionic groups X of from about 1:1 to about 1:2. However, for example, by appropriate copolymerization of cationic, nonionic (i.e. containing the group L-X), and mixed cationic/nonionic monomers, the ratio of cationic groups M to nonionic groups X can be varied. The ratio of groups M to groups X can usually range from about 2:1 to about 1:10. In preferred cationic polymers, the ratio is from about 1:1 to about 1:5. The polymers formed from such copolymerization are typically random, i.e. the cationic, nonionic and mixed cationic/nonionic monomers copolymerize in a nonrepeating sequence.

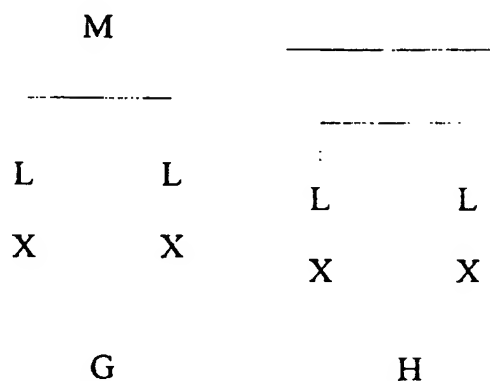
The units which contain groups M and groups L-X can comprise 100% of the cationic polymers of the present invention. However, inclusion of other units (preferably nonionic) in the polymers is also permissible. Examples of other units include acrylamides, vinyl ethers and those containing unquaternized tertiary amine groups (M¹) containing an N centre. These other units can comprise from 0% to about 90% of the polymer (from about 10% to 100% of the polymer being units containing M and L-X groups, including M¹-L-X groups). Normally, these other units comprise from 0% to about 50% of the polymer (from about 50% to 100% of the polymer being units containing M and L-X groups).

The number of groups M and L-X each usually ranges from about 2 to about 200. Typically the number of groups M and L-X are each from about 3 to about 100. Preferably, the number of groups M and L-X are each from about 3 to about 40.

Other than moieties for connecting groups M and X, or for attachment to the polymer backbone, hydrophilic chain L usually consists entirely of the polyoxyalkylene moiety $-(R'O)_m(CH_2CH_2O)_n-$. The moieties $-(R'O)_m-$ and $-(CH_2CH_2O)_n-$ of the polyoxyalkylene moiety can be mixed together, or preferably form blocks of $-(R'O)_m-$ and $-(CH_2CH_2O)_n-$ moieties. R' is preferably C₃H₆

(propylene); m is preferably from 0 to about 5, and most preferably 0; i.e. the polyoxyalkylene moiety consists entirely of the moiety $-(CH_2CH_2O)_m-$. The moiety $-(CH_2CH_2O)_m-$ preferably comprises at least about 85% by weight of the polyoxyalkylene moiety, and most preferably 100% by weight (m is 0). For the moiety $-(CH_2CH_2O)_n-$, n is usually from about 3 to about 100. Preferably, n is from about 12 to about 42.

A plurality (2 or more) of moieties -L-X can also be hooked together and attached to group M or to the polymer backbone, examples of which are represented by the following general structures G and H:



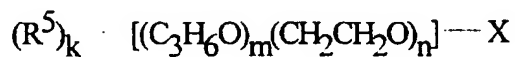
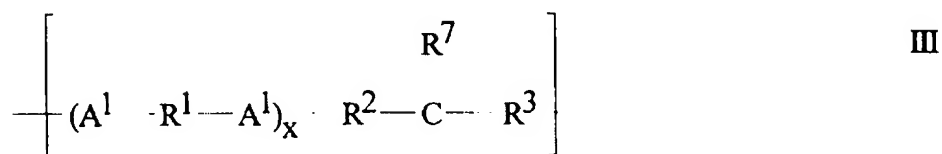
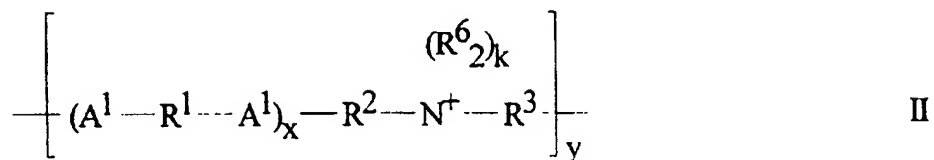
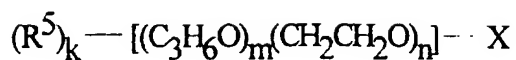
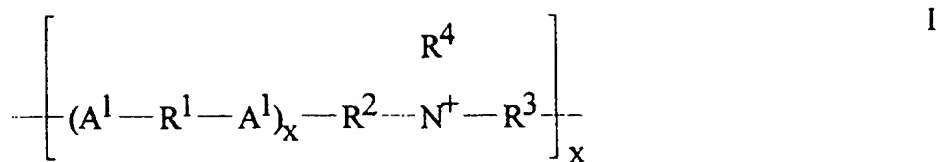
Structures such as G and H can be formed, for example, by reacting glycidol with group M or with the polymer backbone, and ethoxylating the subsequently formed hydroxy groups.

Representative classes of cationic polymers of the present invention are as follows:

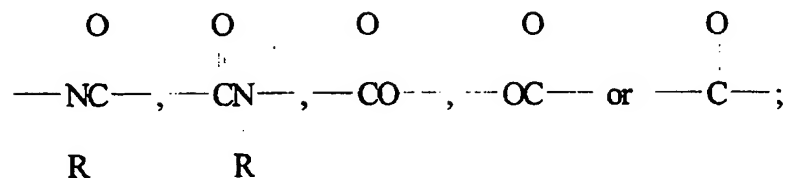
A. Polyurethane, Polyester, Polyether, Polyamide or like Polymers.

One class of suitable cationic polymers are derived from polyurethanes, polyesters, polyethers, polyamides and the like. These polymers comprise units selected from those having formulas I, II and III:

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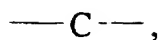
wherein A¹ is



X is 0 or 1; R is H or C₁-C₄ alkyl or hydroxyalkyl; R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, cycloalkylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed with A¹; when x is 1, R² is -R⁵- except when A¹ is

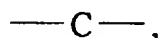
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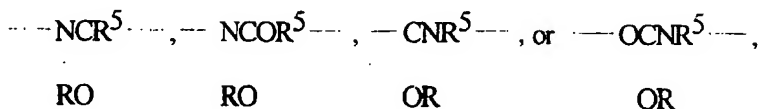
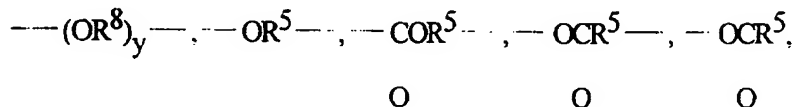


or is $-(\text{OR}^8)_y$ - or $-\text{OR}^5$ - provided that no O-O or N-O bonds are formed with A^1 , and R^3 is $-\text{R}^5$ - except when A^1 is

O

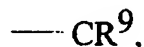


or is $-(\text{R}^8\text{O})_y$ - or $-\text{R}^5\text{O}$ - provided that no O-O or O-N bonds are formed with A^1 ; when x is 0, R^2 is



and R^3 is $-\text{R}^5$ -; R^4 is C_1 - C_4 alkyl or hydroxyalkyl, or the moiety $-(\text{R}^5)_k$ -
 $[(\text{C}_3\text{H}_6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]\text{-X}$; R^5 is C_1 - C_{12} alkylene, hydroxyalkylene, alkenylene,
 arylene, or alkarylene; each R^6 is C_1 - C_4 alkyl or hydroxyalkyl, or the moiety $-(\text{CH}_2)_r\text{-A}^2\text{-(CH}_2)_s\text{-}$, wherein A^2 is $-\text{O}-$ or $-\text{CH}_2-$; R^7 is H or R^4 ; R^8 is C_2 - C_3
 alkylene or hydroxyalkylene; X is H,

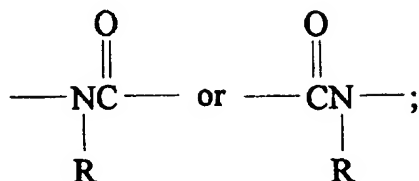
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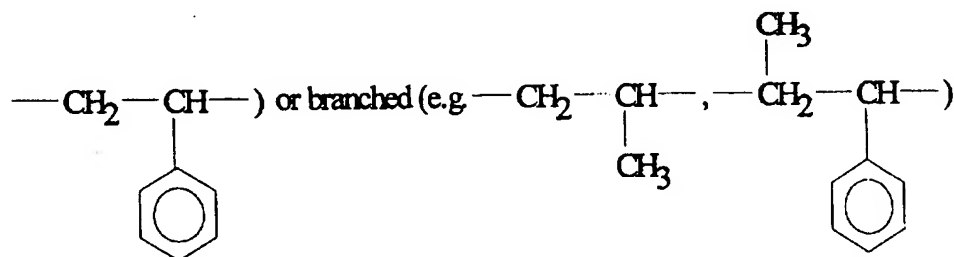
$-\text{R}^9$ or a mixture thereof, wherein R^9 is C_1 - C_4 alkyl or hydroxyalkyl; k is 0 or 1; m and n are numbers such that the moiety $-(\text{CH}_2\text{CH}_2\text{O})_n\text{-}$ comprises at least about 85% by weight of the moiety $[(\text{C}_3\text{H}_6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]\text{-}$; m is from 0 to about 5; n is at least about 3; r is 1 or 2, s is 1 or 2, and $r + s$ is 3 or 4; y is from 2 to about 20; the

number of u, v and w are such that there are at least 2 N⁺ centers and at least 2 X groups.

In the above formulas, A¹ is preferably



A² is preferably -O-; x is preferably 1; and R is preferably H. R¹ can be linear (e.g. -CH₂-CH₂-CH₂-,



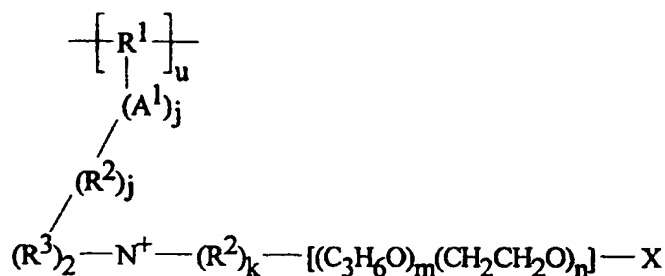
alkylene, hydroxyalkylene, alkenylene, cycloalkylene, alkarylene or oxyalkylene; when R¹ is a C₂-C₃ oxyalkylene moiety, the number of oxyalkylene units is preferably from about 2 to about 12; R¹ is preferably C₂-C₆ alkylene or phenylene, and most preferably C₂-C₆ alkylene (e.g. ethylene, propylene, hexamethylene). R² is preferably -OR⁵- or -(OR⁸)_y-; R³ is preferably -R⁵O- or -(OR⁸)_y-; R⁴ and R⁶ are preferably methyl. Like R¹, R⁵ can be linear or branched, and is preferably C₂-C₃ alkylene; R⁷ is preferably H or C₁-C₃ alkyl; R⁸ is preferably ethylene; R⁹ is preferably methyl; X is preferably H or methyl; k is preferably 0; m is preferably 0, r and s are each preferably 2; y is preferably from 2 to about 12.

In the above formulas, n is preferably at least about 6 when the number of N⁺ centers and X groups is 2 or 3; n is most preferably at least about 12, with a typical range of about 12 to about 42 for all ranges of u + v + w. For homopolymers (v and w are 0), u is preferably from about 3 to about 20. For random copolymers (u is at least 1 or preferably 0), v and w are each preferably from about 3 to about 40.

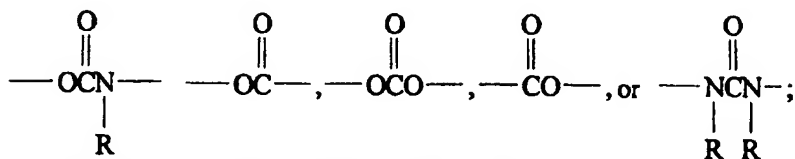
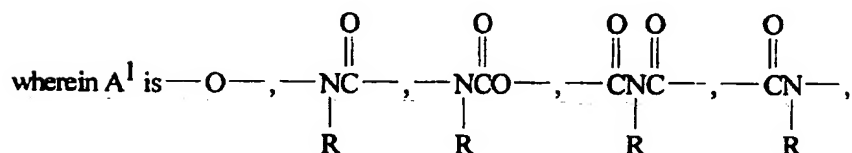
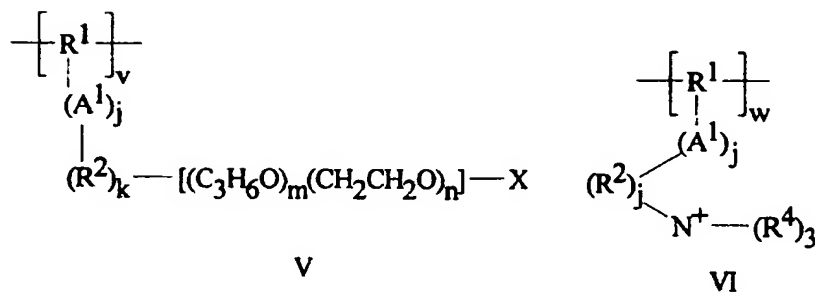
B. Polyacrylate, Polyacrylamide, Polyvinylether or

Like Polymers

Another class of suitable cationic polymers are derived from polyacrylates, polyacrylamides, polyvinylethers and the like. These polymers comprise units selected from those having formulas IV, V and VI.

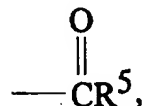


IV



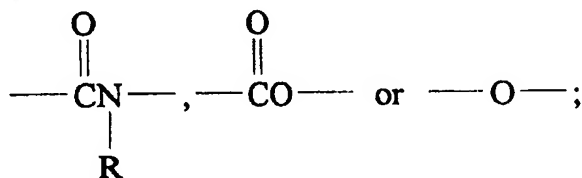
R is H or C₁-C₄ alkyl or hydroxyalkyl; R¹ is substituted C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or C₂-C₃ oxyalkylene; each R² is C₁-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene; each R³ is C₁-C₄ alkyl or hydroxyalkyl, the moiety -(R²)_k[(C₃H₆O)_m(CH₂CH₂O)_n]-X, or together form the moiety -(CH₂)_r-A²-(CH₂)_s-, wherein A² is -O- or -CH₂-; each R⁴

is C₁-C₄ alkyl or hydroxyalkyl, or two R⁴ together form the moiety -(CH₂)_r-A²-(CH₂)_s-; X is H,



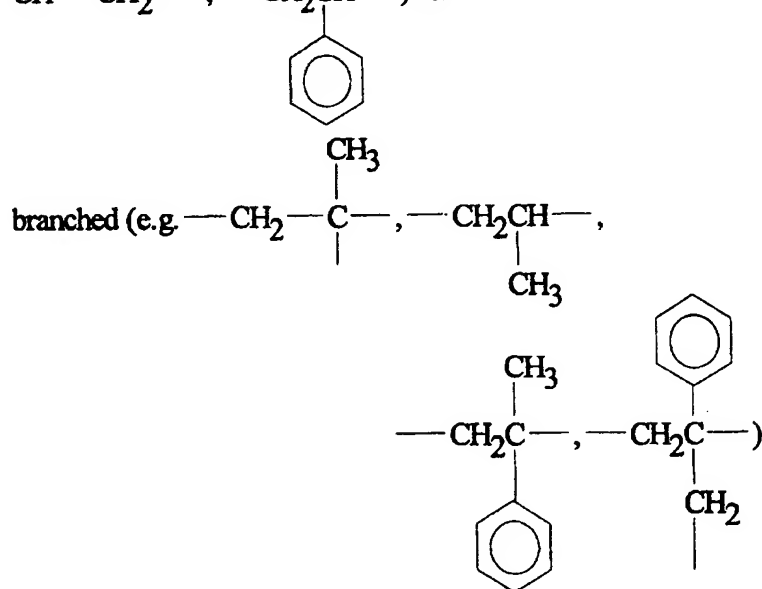
-R⁵ or mixture thereof, wherein R⁵ is C₁-C₄ alkyl or hydroxalkyl; j is 1 or 0; k is 1 or 0; m and n are numbers such that the moiety -(CH₂CH₂O)_n- comprises at least about 85% by weight of the moiety -[(C₃H₆O)_m(CH₂CH₂O)_n]-; m is from 0 to about 5; n is at least about 3; r is 1 or 2, s is 1 or 2 and r + s is 3 or 4; the number of u, v and w are such that there are at least 2N⁺ centres and at least 2 X groups.

In the above formulas, A¹ is preferably

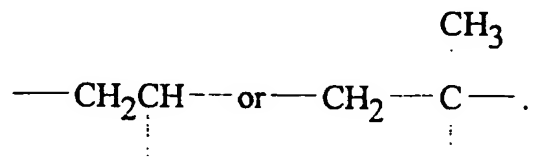


A² is preferably -O-; R is preferably H. R¹ can be linear

(e.g. —CH₂—CH—CH₂—, —CH₂CH—) or



substituted alkylene, hydroxyalkylene, alkenylene, alkarylene or oxyalkylene; R^1 is preferably substituted C_2-C_6 alkylene or substituted C_2-C_3 oxyalkylene, and most preferably

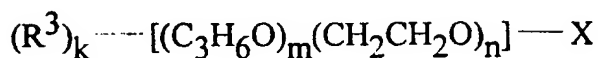
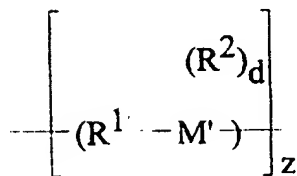
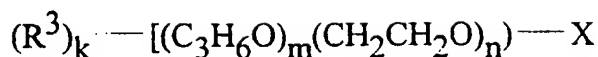
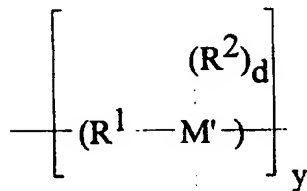
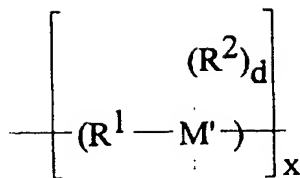


Each R^2 is preferably C_2-C_3 alkylene, each R^3 and R^4 are preferably methyl; R^5 is preferably methyl; X is preferably H or methyl; j is preferably 1; k is preferably 0; m is preferably 0; r and s are each preferably 2.

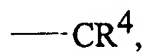
In the above formulas, n, u, v and w can be varied according to the n, u, v and w for the polyurethane and like polymers.

C. Polyalkyleneamine, Polyalkyleneimine or like polymers.

Another class of suitable cationic polymers are derived from polyalkyleneamines, polyalkyleneimines and the like. These polymers comprise units selected from those having formulas VII and VIII and IX.



wherein R^1 is C_2 - C_{12} alkylene, hydroxyalkylene, alkenylene, cycloalkylene, arylene or alkarylene, or a C_2 - C_3 oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R^2 is C_1 - C_4 alkyl or hydroxyalkyl, or the moiety $-(R^3)_k-[(C_3H_6O)_m(CH_2CH_2O)_n]-X$; R^3 is C_1 - C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene; M' is an N^+ or N centre; X is H,



O

$-R^4$ or mixture thereof, wherein R^4 is C_1 - C_4 alkyl or hydroxyalkyl; d is 1 when M' is N^+ and is 0 when M' is N ; e is 2 when M' is N^+ and is 1 when M' is N ; k is 1 or 0; m and n are numbers such that the moiety

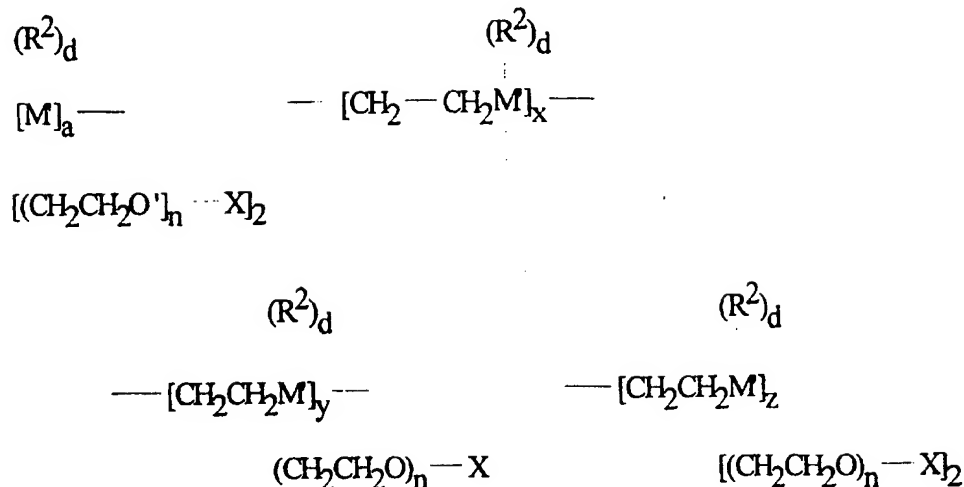
$-(\text{CH}_2\text{CH}_2\text{O})_n-$ comprises at least about 85% by weight of the moiety $-[(\text{C}_3\text{H}_6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]-$; m is from 0 to about 5; n is at least about 3; the number of x , y and z are such that there are at least $2\text{M}'$ groups, at least 2N^+ centres and at least 2 X groups.

In the above formulas, R^1 can be varied like R^1 of the polyurethane and like polymers; each R^2 is preferably methyl or the moiety $-(\text{R}^3)_k-$ $[(\text{C}_3\text{H}_6\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]-\text{X}$; R^3 is preferably C_2 - C_3 alkylene; R^4 is preferably methyl; X is preferably H; k is preferably 0; m is preferably 0.

In the above formulas, n is preferably at least about 6 when the number of M' and X groups is 2 or 3; n is most preferably at least about 12, with a typical range of from about 12 to about 42 for all ranges of $x + y + z$. Typically, $x + y + z$ is from 2 to about 40 and preferably from 2 to about 20. For short chain length polymers, $x + y + z$ can range from 2 to 9 with from 2 to 9 N^+ centres and from 2 to 11 X groups. For long chain length polymers, $x + y + z$ is at least 10, with a preferred range of from 10 to about 42. For the short and long chain length polymers, the M' groups are typically a mixture of from about 50 to 100% N^+ centres and from 0 to about 50% N centres.

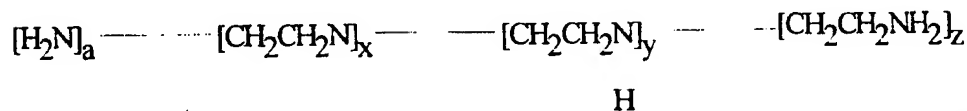
Preferred cationic polymers within this class are derived from the C_2 - C_3 polyalkyleneamines ($x + y + z$ is from 2 to 9) and polyalkyleneimines ($x + y + z$ is at least 10, preferably from 10 to about 42). Particularly preferred cationic polyalkyleneamines and polyalkyleneimines are the cationic polyethyleneamines (PEA's) and polyethyleneimines (PEI's). These preferred cationic polymers comprise units having the general formula:

36



wherein R^2 (preferably methyl), M' , X , d , x , y , z and n are defined as before; a is 1 or 0.

Prior to ethoxylation, the PEAs used in preparing cationic polymers of the present invention have the following general formula:

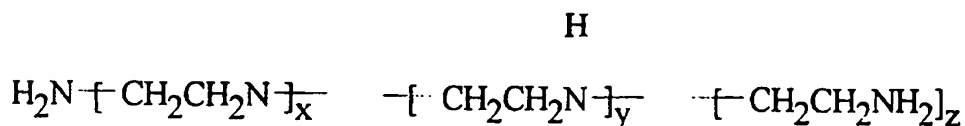


wherein $x + y + z$ is from 2 to 9, and a is 0 or 1 (molecular weight of from about 100 to about 400). Each hydrogen atom attached to each nitrogen atom represents an active site for subsequent ethoxylation. For preferred PEAs, $x + y + z$ is from about 3 to about 7 (molecular weight is from about 140 to about 310). These PEA's can be obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See US Pat. No. 2,792,372 to Dickson, issues May 14, 1957, which describes the preparation of PEAs.

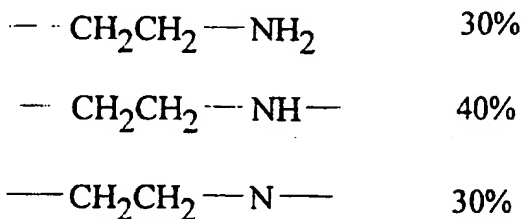
The minimum degree of ethoxylation required for preferred clay soil removal/anti-redeposition performance can vary depending upon the number of units in the PEA. Where $y + z$ is 2 or 3, n is preferably at least about 6. Where $y + z$ is from 4 to 9,

suitable benefits are achieved when n is at least about 3. For preferred cationic PEAs, n is at least about 12, with a typical range of about 12 to about 42.

The PEIs used in preparing the polymers of the present invention have a molecular weight of at least about 440 prior to ethoxylation, which represents at least about 10 units. Preferred PEIs used in preparing these polymers have a molecular weight of from about 600 to about 1800. The polymer backbone of these PEIs can be represented by the general formula:



wherein the sum of x, y, and z represents a number of sufficient magnitude to yield a polymer having the molecular weights previously specified. Although linear polymer backbones are possible, branch chains can also occur. The relative proportions of primary, secondary and tertiary amine groups present in the polymer can vary, depending on the manner of preparation. The distribution of amine groups is typically as follows:



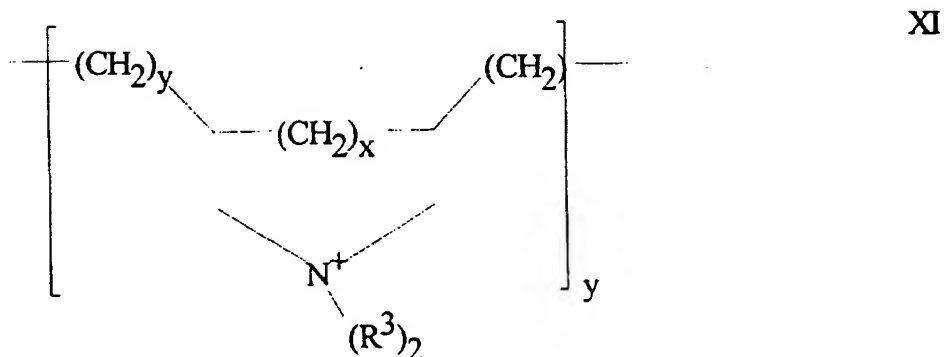
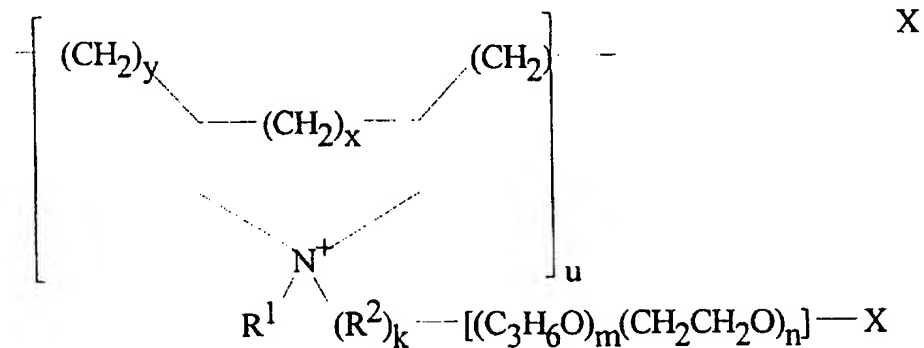
Each hydrogen atom attached to each nitrogen atom of the PEI represents an active site for subsequent ethoxylation. These PEIs can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing PEIs are disclosed in US Pat. No. 2,182,306 to Ulrich et al., issued Dec. 5, 1939; US Pat No. 3,033,746 to Mayle et al., issued May 8, 1962; US Pat. No. 2,208,095 to Esselmann et al., issued July 16, 1940; US Pat. No.

2,806,839 to Crowther, issued Sept. 17, 1957; and US Pat. No. 2,533,696 to Wilson, issued May 21, 1951 (all herein incorporated by reference).

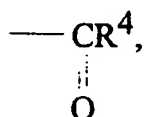
As defined in the preceding formulas, n is at least about 3 for the cationic PEIs. However, it should be noted that the minimum degree of ethoxylation required for suitable clay soil removal/anti-redeposition performance can increase as the molecular weight of the PEI increases, especially much beyond about 1800. Also, the degree of ethoxylation for preferred polymers increases as the molecular weight of the PEI increases. For PEIs having a molecular weight of at least about 600, n is preferably at least about 12, with a typical range of from about 12 to about 42. For PEIs having a molecular weight of at least 1800, n is preferably at least about 24, with a typical range of from about 24 to about 42.

D. Diallylamine Polymers

Another class of suitable cationic polymers are those derived from the diallylamines. These polymers comprise units selected from those having formulas X and XI:



wherein R^1 is C_1 - C_4 alkyl or hydroxyalkyl, or the moiety $-(R^2)_k-$ $[(C_3H_6O)_m(CH_2CH_2O)_n]-X$; R^2 is C_1 - C_{12} alkylene, hydroxyalkylene, alkylene, arylene or alkarylene; each R^3 is C_1 - C_4 alkyl or hydroxyalkyl, or together form the moiety $-(CH_2)_r-A-(CH_2)_s-$, wherein A is $-O-$ or $-CH_2-$; X is H,



$-R^4$ or mixture thereof, wherein R^4 is C_1 - C_4 alkyl or hydroxyalkyl; k is 1 or 0; m and n are numbers such that the moiety $-(CH_2CH_2O)_n-$ comprises at least about 85% by weight of the moiety $-[(C_3H_6O)_m(CH_2CH_2O)_n]-$; m is from 0 to about 5; n is at least about 3; r is 1 or 2, s is 1 or 2, and r + s is 3 or 4; x is 1 or 0; y is 1 when x is 0 and 0 when x is 1; the number of u and v are such that there are at least $2N+$ centres and at least 2 X groups.

In the above formulas, A is preferably $-O-$; R^1 is preferably methyl; each R^2 is preferably C_2 - C_3 alkylene; each R^3 is preferably methyl; R^4 is preferably methyl; X is preferably H; k is preferably 0; m is preferably 0; r and s are each preferably 2.

In the above formulas, n is preferably at least about 6 when the number of $N+$ centres and X groups are each 2 or 3, n is preferably at least 12, with a typical range of from about 12 to about 42 for all range of u + v. Typically, v is 0, and u is from 2 to about 40, and preferably from 2 to about 20.

Additional detergent components

The detergent compositions or components thereof in accord with the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition or component, and the precise nature of the washing operation for which it is to be used.

The compositions or components thereof, of the invention preferably contain one or more additional detergent components selected from additional surfactants,

additional bleaches, bleach catalysts, alkalinity systems, builders, organic polymeric compounds, enzymes, suds suppressors, lime soap dispersants, additional soil suspension and anti-redeposition agents soil releasing agents, perfumes and corrosion inhibitors.

Additional surfactant

The detergent compositions or components thereof in accord with the invention preferably contain an additional surfactant selected from anionic, nonionic, cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Where present, ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic surfactant

The detergent compositions or compositions thereof in accord with the present invention preferably comprise an additional anionic surfactant. Essentially any anionic surfactants useful for deterative purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are

also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C₁₀-C₁₈ alkyl sulfates, more preferably the C₁₁-C₁₅ branched chain alkyl sulfates and the C₁₂-C₁₄ linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₁₀-C₁₈ alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₁₁-C₁₈, most preferably C₁₁-C₁₅ alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_2O)_xCH_2COO-M^+$ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R₃ is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula $R-CON(R^1)CH_2COOM$, wherein R is a C₅-C₁₇ linear or branched alkyl or alkenyl group, R¹ is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Alkoxyated nonionic surfactant

Essentially any alkoxyated nonionic surfactants are suitable herein. The ethoxyated and propoxyated nonionic surfactants are preferred.

Preferred alkoxyated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic alkoxyated alcohol surfactant

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein: R^1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{31} hydrocarbyl, preferably straight-chain C_5 - C_{19} alkyl or alkenyl, more preferably straight-chain C_9 - C_{17} alkyl or alkenyl, most preferably straight-chain C_{11} - C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

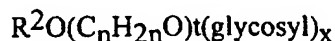
Nonionic fatty acid amide surfactant

Suitable fatty acid amide surfactants include those having the formula: $R^6CON(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10} - C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl amphocarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions or components thereof in accord with the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, each R¹ is typically C₁-C₃ alkyl, and R² is a C₁-C₅ hydrocarbyl group. Preferred betaines are C₁₂-C₁₈ dimethyl-ammonio hexanoate and the C₁₀-C₁₈ acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Cationic surfactants

Suitable cationic surfactants to be used in the detergent compositions or components thereof herein include the quaternary ammonium surfactants selected from mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Another suitable group of cationic surfactants which can be used in the detergent compositions or components thereof herein are cationic ester surfactants. The cationic ester surfactant is a, preferably water dispersible, compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group.

Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

In one preferred aspect the ester linkage and cationically charged group are separated from each other in the surfactant molecule by a spacer group consisting of a chain comprising at least three atoms (i.e. of three atoms chain length), preferably from three to eight atoms, more preferably from three to five atoms, most preferably three

atoms. The atoms forming the spacer group chain are selected from the group consisting of carbon, nitrogen and oxygen atoms and any mixtures thereof, with the proviso that any nitrogen or oxygen atom in said chain connects only with carbon atoms in the chain. Thus spacer groups having, for example, -O-O- (i.e. peroxide), -N-N-, and -N-O- linkages are excluded, whilst spacer groups having, for example -CH₂-O-CH₂- and -CH₂-NH-CH₂- linkages are included. In a preferred aspect the spacer group chain comprises only carbon atoms, most preferably the chain is a hydrocarbyl chain.

Water-soluble builder compound

The detergent compositions or components thereof in accord with the present invention preferably contain a water-soluble builder compound, typically present in detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, phosphates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials

such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

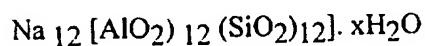
Partially soluble or insoluble builder compound

The detergent compositions or compositions thereof in accord with the present invention may contain a partially soluble or insoluble builder compound, typically present in detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates.

Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula



wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86} [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$.

Another preferred aluminosilicate zeolite is zeolite MAP builder.

The zeolite MAP can be present at a level of from 1% to 80%, more preferably from 15% to 40% by weight of the compositions.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

In a preferred aspect the zeolite MAP detergent builder has a particle size, expressed as a d_{50} value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres.

The d_{50} value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional analytical techniques such as microscopic determination using a

scanning electron microscope or by means of a laser granulometer. Other methods of establishing d_{50} values are disclosed in EP 384070A.

Heavy metal ion sequestrant

The detergent compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1.1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-

3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.

Bleach catalyst

The oxygen-releasing bleach system can contain a transition metal containing bleach catalyst.

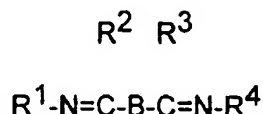
One suitable type of bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

The bleach catalysts useful herein may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $\text{Mn}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})(\text{OCH}_3)_3\text{-(PF}_6\text{)}$.

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with an non-(macro)-cyclic ligand. Said ligands are of the formula:



wherein R^1 , R^2 , R^3 , and R^4 can each be selected from H, substituted alkyl and aryl groups such that each $\text{R}^1\text{-N}=\text{C}-\text{R}^2$ and $\text{R}^3\text{-C}=\text{N}-\text{R}^4$ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S, CR^5R^6 , NR^7 and $\text{C}=\text{O}$, wherein R^5 , R^6 , and R^7 can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe, -bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include $\text{Co}(2,2'\text{-bispyridylamine})\text{Cl}_2$, $\text{Di(isothiocyanato)bispyridylamine-cobalt(II)}$, $\text{tris(dipyridylamine-cobalt(II)) perchlorate}$, $\text{Co}(2,2'\text{-bispyridylamine})_2\text{O}_2\text{ClO}_4$, $\text{Bis-(2,2'-bispyridylamine) copper(II) perchlorate}$, $\text{tris(di-2-pyridylamine) iron(II) perchlorate}$, and mixtures thereof.

Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{N}_4)^+$ and $[\text{Bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2]\text{-(ClO}_4\text{)}_3$.

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

The bleach catalyst is typically used in a catalytically effective amount in the compositions and processes herein. By "catalytically effective amount" is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance bleaching and removal of the stain or stains of interest from the target substrate. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some users elect to use very hot water; others use warm or even cold water in laundering operations. Of course, the catalytic performance of the bleach catalyst will be affected by such considerations, and the levels of bleach catalyst used in fully-formulated detergent and bleach compositions can be appropriately adjusted. As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 1 ppm to about 200 ppm of the catalyst species in the wash liquor. To illustrate this point further, on the order of 3 micromolar manganese catalyst is effective at 40°C, pH 10 under European conditions using perborate and a bleach precursor. An increase in concentration of 3-5 fold may be required under U.S. conditions to achieve the same results.

Enzyme

Another preferred ingredient useful in the detergent compositions or components thereof is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α -amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of *Humicola* sp., *Thermomyces* sp. or *Pseudomonas* sp. including *Pseudomonas pseudoalcaligenes* or *Pseudomonas fluorescens*. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from *Humicola lanuginosa* and expressing the gene in *Aspergillus oryza*, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from

Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions or components thereof in accord with the invention, and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein, not being an quaternised ethoxylated (poly) amine clay-soil removal/ anti-redeposition agent in accord with the invention.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 1000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 2000 to 100,000, especially 40,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Suds suppressing system

The detergent compositions of the invention; when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24

carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyl diamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises

- (a) antifoam compound, preferably silicone antifoam compound, most preferably
 - a silicone antifoam compound comprising in combination
 - (i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and
 - (ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

- (b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

- (c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

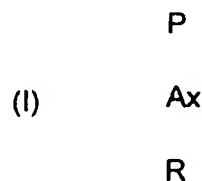
Polymeric dye transfer inhibiting agents

The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof, whereby these polymers can be cross-linked polymers.

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :



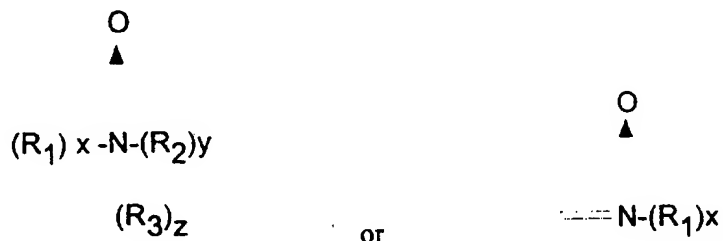
wherein P is a polymerisable unit, and



A is NC, CO, C, -O-, -S-, -N-; x is 0 or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof where to the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides where to the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides

wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Suitable herein are copolymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

d) Polyvinylloxazolidone

The detergent compositions herein may also utilize polyvinylloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinylloxazolidones have an average molecular weight of from 2,500 to 400,000.

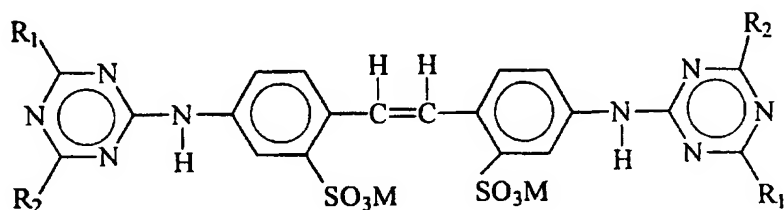
e) Polyvinylimidazole

The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical brightener

The detergent compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morpholino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid

disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Polymeric Soil Release Agent

Known polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate

("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C₁-C₄ alkyl celluloses and C₄ hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Additional classes of SRA's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl

groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.;

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

Near neutral wash pH detergent formulation

While the detergent compositions of the present invention are operative within a wide range of wash pHs (e.g. from about 5 to about 12), they are particularly suitable when formulated to provide a near neutral wash pH, i.e. an initial pH of from about 7.0 to about 10.5 at a concentration of from about 0.1 to about 2% by weight in water at 20°C. Near neutral wash pH formulations are better for enzyme stability and for preventing stains from setting. In such formulations, the wash pH is preferably from about 7.0 to about 10.5, more preferably from about 8.0 to about 10.5, most preferably from 8.0 to 9.0.

Preferred near neutral wash pH detergent formulations are disclosed to European Patent Application 83.200688.6, filed May 16, 1983, J.H.M. Wertz and P.C.E. Goffinet.

Highly preferred compositions of this type also preferably contain from about 2 to about 10% by weight of citric acid and minor amounts (e.g., less than about 20% by weight) of neutralizing agents, buffering agents, phase regulants, hydrotropes, enzymes, enzyme stabilizing agents, polyacids, suds regulants, opacifiers, anti-oxidants, bactericides, dyes, perfumes and brighteners, such as those described in US Patent 4,285,841 to Barrat et al., issued August 25, 1981 (herein incorporated by reference).

Form of the compositions

The detergent component of the invention can be made via a variety of methods, including dry-mixing and agglomerating of the various compounds comprised in the detergent component.

The detergent component preferably forms part of a detergent composition. The compositions in accordance with the invention can take a variety of physical forms including granular, tablet, flake, pastille and bar forms. The compositions are particularly the so-called concentrated granular detergent compositions adapted to be added to a washing machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

The compositions in accord with the present invention can also be used in or in combination with bleach additive compositions, for example comprising chlorine bleach.

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation. The quaternised clay-soil removal/ anti-redeposition agent in accord with the present invention can be added to the other detergent components by dry-mixing, agglomeration (preferably combined with a carrier material) or as a spray-dried component.

The mean particle size of the components of granular compositions in accordance with the invention, comprising the water-soluble cationic clay-soil removal/anti-redeposition compounds, should preferably be such that no more than 15% of the particles are greater than 1.8mm in diameter and not more than 15% of the particles are less than 0.25mm in diameter. Preferably the mean particle size is such that from 10% to 50% of the particles has a particle size of from 0.2mm to 0.7mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of sieves, preferably Tyler sieves. The weight fractions thereby obtained are plotted against the

aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 600 g/litre, more preferably from 650 g/litre to 1200 g/litre. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

Compacted solids may be manufactured using any suitable compacting process, such as tableting, briquetting or extrusion, preferably tableting. Preferably tablets for use in dish washing processes, are manufactured using a standard rotary tableting press using compression forces of from 5 to 13 KN/cm², more preferably from 5 to 11 KN/cm² so that the compacted solid has a minimum hardness of 176N to 275N, preferably from 195N to 245N, measured by a C100 hardness test as supplied by I. Holland instruments. This process may be used to prepare homogeneous or layered tablets of any size or shape. Preferably tablets are symmetrical to ensure the uniform dissolution of the tablet in the wash solution.

Laundry washing method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein

an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 10g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

The dispensing device containing the detergent product is placed inside the drum before the commencement of the wash, before, simultaneously with or after the washing machine has been loaded with laundry. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use with the composition of the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a

type commonly known as the "granulette". Another preferred dispensing device for use with the compositions of this invention is disclosed in PCT Patent Application No. WO94/11562.

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

Machine dishwashing method

Any suitable methods for machine dishwashing or cleaning soiled tableware, particularly soiled silverware are envisaged.

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, hollowware, silverware and cutlery and mixtures thereof, with an aqueous liquid having dissolved or dispensed therein an effective amount of a machine dishwashing composition in accord with the invention. By an effective

amount of the machine dishwashing composition it is meant from 8g to 60g of product dissolved or dispersed in a wash solution of volume from 3 to 10 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods.

Packaging for the compositions

Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in European Application No. 94921505.7.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C ₁₂ alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
C _{xy} AS	:	Sodium C _{1x} - C _{1y} alkyl sulfate
C ₄₆ SAS	:	Sodium C ₁₄ - C ₁₆ secondary (2,3) alkyl sulfate
C _{xy} EzS	:	Sodium C _{1x} -C _{1y} alkyl sulfate condensed with z moles of ethylene oxide
C _{xy} Ez	:	C _{1x} -C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
QAS	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ - C ₁₄
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils
CFAA	:	C ₁₂ -C ₁₄ (coco) alkyl N-methyl glucamide
TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
TPKFA	:	C ₁₂ -C ₁₄ topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate
TSPP	:	Tetrasodium pyrophosphate
Zeolite A	:	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (AlO ₂ SiO ₂) ₁₂ .27H ₂ O having a primary

		particle size in the range from 0.1 to 10 micrometers
Zeolite MAP	:	Hydrated sodium aluminosilicate zeolite MAP having a silicon to aluminium ratio of 1.07
NaSKS-6	:	Crystalline layered silicate of formula δ - $\text{Na}_2\text{Si}_2\text{O}_5$
Citric acid	:	Anhydrous citric acid
Borate	:	Sodium borate
Carbonate	:	Anhydrous sodium carbonate with a particle size between 200 μm and 900 μm
Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400 μm and 1200 μm
Silicate	:	Amorphous Sodium Silicate ($\text{SiO}_2:\text{Na}_2\text{O} = 2.0:1$)
Sodium sulfate	:	Anhydrous sodium sulfate
Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 μm and 850 μm
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid. average molecular weight about 70,000
AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
CMC	:	Sodium carboxymethyl cellulose
Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
Protease	:	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
Alcalase	:	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
Cellulase	:	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
Amylase	:	Amylolytic enzyme of activity 120KNU/g sold by NOVO Industries A/S under the tradename Termamyl 120T

Lipase	:	Lipolytic enzyme of activity 100KLU/g sold by NOVO Industries A/S under the tradename Lipolase
Endolase	:	Endoglucanase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
Percarbonate	:	Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
NAC-OBS	:	(Nonanamido caproyl) oxybenzene sulfonate in the form of the sodium salt.
NACA	:	6 nonylamino - 6 oxo - capronic acid.
NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt
TAED	:	Tetraacetythylenediamine
Mn catalyst	:	$\text{Mn}^{\text{IV}}_2(\text{m-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, as described in U.S. Pat. Nos. 5,246,621 and 5,244,594.
DTPA	:	Diethylene triamine pentaacetic acid
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
Photoactivated	:	Sulfonated Zinc Phthlocyanine encapsulated in bleach dextrin soluble polymer
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyry)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate
HEDP	:	1,1-hydroxyethane diphosphonic acid
EDDS	:	Ethylenediamine-N, N'-disuccinic acid
QEA1	:	$\text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)(\text{CH}_3) \text{-N}^+ \text{-C}_6\text{H}_{12} \text{-N}^+ \text{-}(\text{CH}_3) \text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)$, wherein n=from 20 to 30
QEA2	:	$\text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)(\text{CH}_3) \text{N}^+ \text{R}_1$, wherein R_1 is $\text{C}_4\text{-C}_{12}$ alkyl group and n=from 20 to 30

QEA3	:	tri{(bis((C ₂ H ₅ O)-(C ₂ H ₄ O) _n)(CH ₃)-N ⁺)- (CONC ₃ H ₆))-C ₃ H ₆ O, wherein n=from 20 to 26
PEGX	:	Polyethylene glycol, with a molecular weight of x
PEO	:	Polyethylene oxide, with a molecular weight of 50,000
TEPAE	:	Tetraethylenepentaamine ethoxylate
PVP	:	Polyvinylpyrrolidone polymer
PVNO	:	Polyvinylpyridine N-oxide
PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole
SRP 1	:	Sulfobenzoyl and capped esters with oxyethylene oxy and terephthaloyl backbone
SRP 2	:	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
Wax	:	Paraffin wax

In the following examples all levels are quoted as % by weight of the composition:

Example 1

The following high density granular laundry detergent compositions A to F of particular utility under European machine wash conditions were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
C46AS	1.0	2.0	2.5	-	3.0	4.0
C68AS	3.0	2.0	5.0	7.0	1.0	0.5
QAS	-	-	0.8	-	-	0.8
Zeolite A	18.1	18.1	16.1	18.1	18.1	18.1
Zeolite MAP	-	4.0	3.5	-	-	-
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sodium Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
PB4	9.0	9.0	9.0	9.0	9.0	9.0
NAC OBS	2.5	1.5	3.0	4.0	3.2	2.2
Mn Catalyst	-	0.03	0.07	-	-	-
DTPMP	0.2	0.25	0.25	0.25	0.25	0.25

HEDP	0.3	0.3	0.2	0.2	0.3	0.3
EDDS	-	-	0.4	0.2	-	-
QEA 1	1.0	0.8	0.7	1.2	-	0.5
QEA 2	-	-	-	-	1.0	0.5
Protease	0.2	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.4	0.3	0.1	0.1
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 pp
Brightener 1	0.0	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions G to I of particular utility under European machine wash conditions were prepared in accord with the invention:

	G	H	I
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	2.24	3.89
C25E3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
QAS	0.8	2.0	2.0
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
Zeolite MAP	2.0	-	-
NaSKS-6/citric acid (79:21)	-	10.6	10.6
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	6.8	-	-
Sodium Sulfate	39.8	-	14.3
MA/AA	0.8	1.6	1.6

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CMC	0.2	0.4	0.4
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PB4	5.0	12.7	7.1
TAED	0.5	0.2	-
NAC OBS	1.0	1.3	3.0
DTPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
QEA 1	0.9	1.2	-
QEA 2	-	-	1.0
Protease	0.26	0.85	0.85
Lipase	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28
Amylase	0.4	0.1	0.1
PVP	0.9	1.3	0.8
Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm
Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04
Perfume	0.3	0.3	0.3
Silicone antifoam	0.5	2.4	2.4
Minors/misc to 100%			

Example 3

The following detergent formulations of particular utility under European machine wash conditions were prepared in accord with the invention.

	J	K	L	M
Blown powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	-	27.0	-	20.0
STPP	24.0	-	24.0	-
Sulfate	9.0	6.0	13.0	-
MA/AA	2.0	4.0	6.0	4.0
Silicate	7.0	3.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
QEA 1	0.8	1.0	1.4	0.5
QEA 2	-	-	-	0.5
Brightener	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DTPMP	0.4	0.4	0.2	0.4
Spray on				
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.3	0.3	0.3	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
Sulfate	3.0	3.0	5.0	10.0
Carbonate	6.0	13.0	15.0	14.0
PB1	-	-	-	1.5
PB4	18.0	18.0	10.0	18.5
NAC OBS	3.0	4.2	1.0	2.0
EDDS	-	2.0	2.4	-
Protease	1.0	1.0	1.0	1.0
Lipase	0.4	0.4	0.4	0.2

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Amylase	0.2	0.2	0.2	0.4
Photoactivated bleach	-	-	-	0.15
Total	100.0	100.0	100.0	100.0

Example 4

The following granular detergent formulations were prepared in accord with the invention. Formulation N is particularly suitable for usage under Japanese machine wash conditions. Formulations O to S are particularly suitable for use under US machine wash conditions.

	N	O	P	Q	R	S
Blown powder						
LAS	22.0	5.0	4.0	9.0	8.0	7.0
C45AS	7.0	7.0	6.0	-	-	-
C46AS	-	4.0	3.0	-	-	-
C45E35	-	3.0	2.0	8.0	5.0	4.0
Zeolite A	6.0	16.0	14.0	19.0	16.0	14.0
MA/AA	6.0	3.0	3.0	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sodium Sulfate	7.0	18.3	11.3	24.0	19.3	19.3
Silicate	5.0	1.0	1.0	2.0	1.0	1.0
Carbonate	28.3	9.0	7.0	25.7	8.0	6.0
QEA 1	0.9	0.9	-	-	0.5	1.1
QEA 2	-	-	0.8	1.0	-	-
QEA 3	-	-	0.4	-	-	-
PEG 4000	0.5	1.5	1.5	1.0	1.5	1.0
Sodium oleate	2.0	-	-	-	-	-
DTPA	0.4	-	0.5	-	-	0.5
Brightener	0.2	0.3	0.3	0.3	0.3	0.3
Spray on						
C25E9	1.0	-	-	-	-	-
C45E7	-	2.0	2.0	0.5	2.0	2.0
Perfume	1.0	0.3	0.3	1.0	0.3	0.3
Agglomerates						
C45AS	-	5.0	5.0	-	5.0	5.0
LAS	-	2.0	2.0	-	2.0	2.0
Zeolite A	-	7.5	7.5	-	7.5	7.5
HEDP	-	1.0	-	-	2.0	-

Carbonate	-	4.0	4.0	-	4.0	4.0
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PEG 4000	-	0.5	0.5	-	0.5	0.5
Misc (water etc)	-	2.0	2.0	-	2.0	2.0
Dry additives						
NAC OBS	1.0	2.0	3.0	1.0	3.0	2.0
PB4	-	1.0	4.0	-	5.0	0.5
PB1	6.0	-	-	-	-	-
Percarbonate	-	5.0	12.5	-	-	-
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.5	-	6.0	-	-	0.6
Cumene sulfonic acid	-	2.0	2.0	-	2.0	2.0
Lipase	0.4	0.4	0.4	-	0.4	0.4
Cellulase	0.1	0.2	0.2	-	0.2	0.2
Amylase	0.1	0.3	0.3	-	-	-
Protease	1.0	0.5	0.5	0.5	0.5	0.5
PVPVI	-	0.5	0.5	-	-	-
PVP	0.5	0.5	0.5	-	-	-
PVNO	-	0.5	0.5	-	-	-
SRP1	-	0.5	0.5	-	-	-
Silicone antifoam	-	0.2	0.2	-	0.2	0.2
Total	100.0	100.0	100.0	100.0	100.0	100.0

Example 5

The following granular detergent formulations were prepared in accord with the invention. Formulations W and X are of particular utility under US machine wash conditions. Y is of particular utility under Japanese machine wash conditions

	T	U	V
Blown Powder			
Zeolite A	30.0	22.0	6.0
Sodium Sulfate	19.0	5.0	7.0
MA/AA	3.0	3.0	6.0
LAS	14.0	12.0	22.0
C45AS	8.0	7.0	7.0
Silicate	-	1.0	5.0
Soap	-	-	2.0
Brightener I	0.2	0.2	0.2
QEA I	0.6	2.0	1.0
Carbonate	8.0	16.0	20.0
DTPMP	-	0.4	0.4
Spray On	-	1.0	5.0
C45E7	1.0	1.0	1.0
Dry additives			
HEDP	1.0	-	-
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NAC OBS	-	6.1	4.5
PBI	11.0	5.0	6.0
Sodium Sulfate	-	6.0	-
NACA	5.0	1.0	0.8
Balance (Moisture and Misc)			

Example 6

The following granular detergent compositions of particular utility under European wash conditions were prepared in accord with the invention.

	W	X
Blown powder		
Zeolite A	20.0	-
STPP	-	20.0
LAS	6.0	6.0
C68AS	2.0	2.0
Silicate	3.0	8.0
MA/AA	4.0	2.0
CMC	0.6	0.6
QEA 1	0.9	0.6
QEA 3	0.1	-
Brightener 1	0.2	0.2
DTPMP	0.4	0.4
Spray on		
C45E7	5.0	5.0
Silicone antifoam	0.3	0.3
Perfume	0.2	0.2
Dry additives		
Carbonate	14.0	9.0
NAC OBS	6.0	2.0
NACA	-	4.0
PB4	18.5	13.0
TAED	2.0	
Photoactivated bleach	15 ppm	15 ppm
Protease	1.0	1.0
Lipase	0.2	0.2
Amylase	0.4	0.4
Cellulase	0.1	0.1
Sulfate	10.0	20.0

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Balance (Moisture and Misc.)		
Density (g/litre)	700	700

Example 7

The following detergent compositions, according to the present invention were prepared:

	Y	Z	AA
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodium Sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.2	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
QEA 1	1.0	2.5	0.6
Mn Catalyst	0.03	-	-
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
NAC OBS	6.0	2.0	4.0
TAED	-	2.0	-
PB1	14.0	7.0	10.0
NACA	-	1.0	1.0

Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
EDDS	-	2.0	-
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Misc.)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 8

The following detergent formulations, according to the present invention were prepared:

	BB	CC	DD	EE
LAS	20.0	14.0	24.0	22.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
STPP	30.0	18.0	30.0	22.0
Silicate	9.0	5.0	10.0	8.0
Carbonate	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DTPMP	0.7	1.0	-	-
QEA 1	0.4	1.2	0.5	2.0
QEA 2	0.4	-	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.15	0.05	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
Percarbonate	6.0	5.0	9.0	15.0
PB1	-	2.0	-	-
NAC OBS	4.2	5.0	2.0	1.0
HEDP	-	-	2.3	-
TEAD	2.0	1.0	-	-

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Balance (Moisture and Miscellaneous)				
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Example 9

The following high density granular laundry detergent compositions FF to KK were prepared in accord with the invention:

	FF	GG	HH	II	JJ	KK
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
C46AS	1.0	2.0	2.5	-	3.0	4.0
C68AS	3.0	2.0	5.0	7.0	1.0	0.5
QAS	-	-	0.8	-	-	0.8
Zeolite A	18.1	18.1	16.1	18.1	18.1	18.1
Zeolite MAP	-	4.0	3.5	-	-	-
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sodium Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
PB4	9.0	9.0	9.0	9.0	9.0	9.0
NAC OBS	3.5	1.5	3.0	4.0	3.2	2.2
TEAD	-	1.5	3.0	-	3.0	-
DTPMP	0.25	0.25	0.25	0.25	0.25	0.25

HEDP	0.3	0.3	0.2	0.2	0.3	0.3
EDDS	-	-	0.4	0.2	-	-
QEA 1	1.0	0.8	1.0	1.2	-	0.5
QEA 2	-	-	-	-	1.0	0.5
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.4	0.3	0.1	0.1
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 10

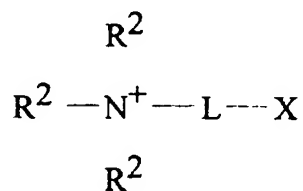
The following detergent compositions, according to the present invention were prepared:

	LL	MM	NN
Blown Powder			
Zeolite A	15.0	15.0	20.0
Sodium Sulfate	5.0	10.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.2	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
QEA I	1.0	2.5	0.6
Mn Catalyst	0.03	-	-
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Citric acid	5.0	2.0	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
NAC OBS	6.0	2.0	4.0
TAED	-	2.0	-
PB1	14.0	7.0	10.0
NACA	-	1.0	1.0

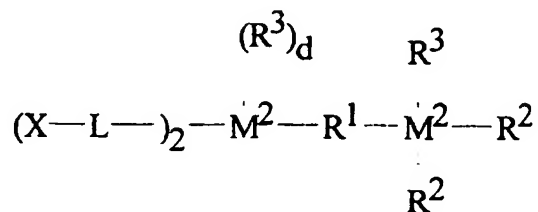
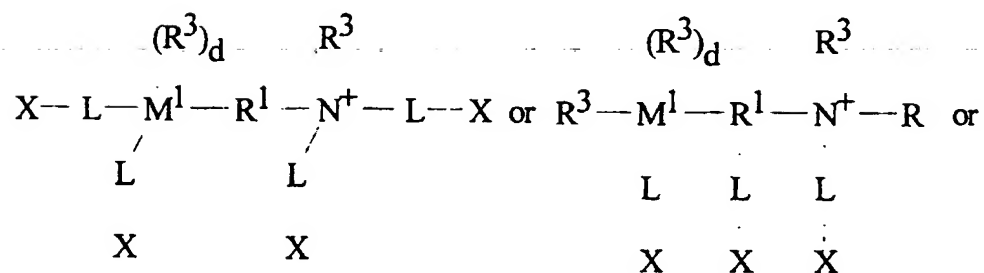
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
EDDS	-	2.0	-
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Misc.)	100.0	100.0	100.0

Claims

1. A granular detergent composition or component thereof comprising
- (a) a hydrophobic organic peroxyacid bleaching system, capable of providing a hydrophobic organic peroxyacid compound; and
 - (b) a water-soluble cationic compound having clay soil removal/anti-redeposition properties, which is selected from the group consisting of:
 - 1) ethoxylated cationic monoamines having the formula:

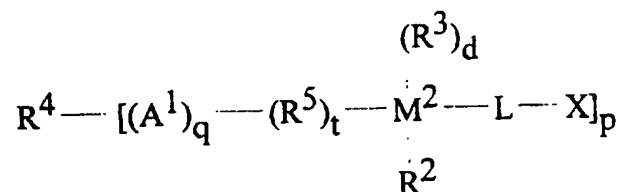


- 2) ethoxylated cationic diamines having the formula:

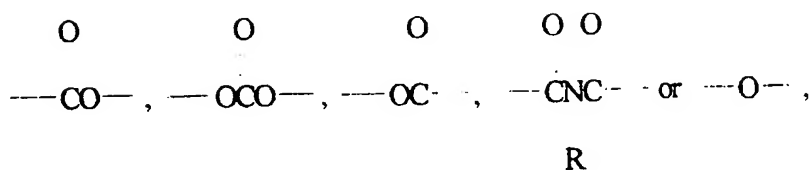
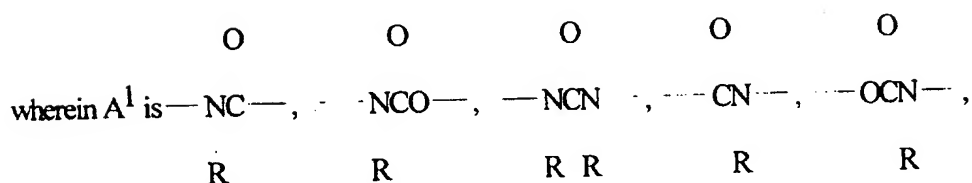


wherein M^1 is an N^+ or N group; each M^2 is an N^+ or N group, and at least one M^2 is an N^+ group;

3) ethoxylated cationic polyamines having the formula:



4) mixtures thereof;



R is H or C_1 - C_4 alkyl or hydroxyalkyl, R^1 is C_2 - C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C_2 - C_3 oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no $O-N$ bonds are formed; each R^2 is C_1 - C_4 alkyl or hydroxyalkyl, the moiety $-L-X$, or two R^2 together form the moiety $-(CH_2)_r-A^2-(CH_2)_s-$, wherein A^2 is $-O-$ or $-CH_2-$, r is 1 or 2, s is 1 or 2 and $r + s$ is 3 or 4; each R^3 is C_1 - C_8 alkyl or hydroxyalkyl, benzyl, the moiety $L-X$, or two R^3 or one R^2 and one R^3 together form the moiety $-(CH_2)_r-A^2-(CH_2)_s-$; R^4 is a substituted C_3 - C_{12} alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl group having p substitution sites; R^5 is C_1 - C_{12} alkenyl, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C_2 - C_3 oxyalkylene moiety having from 2 to about 20 oxyalkylene units

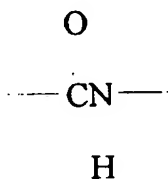
provided that no O-O or O-N bonds are formed; X is a nonionic group selected from the group consisting of H, C₁-C₄ alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof; L is a hydrophilic chain which contains the polyoxyalkylene moiety

$-(R^6O)_m(CH_2CH_2O)_n-$; wherein R⁶ is C₃-C₄ alkylene or hydroxyalkylene and m and n are numbers such that the moiety

$-(CH_2CH_2O)_n-$ comprises at least about 50% by weight of said polyoxyalkylene moiety; d is 1 when M² is N⁺ and is 0 when M² is N; n is at least about 16 for said cationic monoamines, is at least about 6 for said cationic diamines and is at least about 3 for said cationic polyamines; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1.

2. A granular detergent composition according to Claim 1 wherein the ratio of said hydrophobic organic peroxyacid compound to said water-soluble cationic compound is from 20:1 to 1:2.
3. A granular detergent composition according to Claim 1 or 2 wherein said cationic compound is present at a level of from 0.01% to 30% by weight of the detergent composition.
4. A granular detergent composition according to any of Claims 1 to 3 wherein the cationic compound is present at a level of from 0.2% to 3% by weight of the detergent composition.
5. A granular detergent composition or component thereof according to any of Claims 1 to 4 wherein said cationic compound is an ethoxylated cationic monoamine and is characterized in that one R² is methyl, two R² are the moiety L-X, m is 0 and n is at least about 20.
6. A granular detergent composition or component thereof according to any of Claims 1 to 4 wherein said cationic compound is an ethoxylated cationic diamine and is characterized in that R¹ is a C₂-C₆ alkylene.
7. A granular detergent composition or component thereof according to Claim 6 wherein said ethoxylated cationic diamine is characterized in that R¹ is hexamethylene.

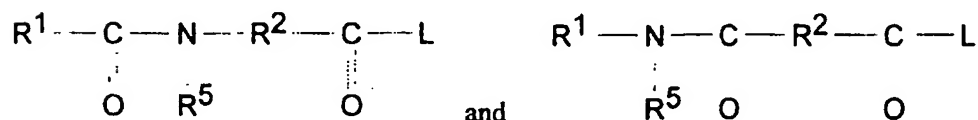
8. A granular detergent composition or component thereof according to Claim 6 or 7, wherein the cationic compounds is characterized in that each R^2 is methyl or the moiety -L-X, each R^3 is methyl and M^1 and each M^2 are an N^+ group.
9. A granular detergent composition or component thereof according to any of Claims 6 to 8 wherein m is 0 and n is at least 12.
10. A detergent composition or component thereof according to any of Claims 1 to 4 wherein said cationic compound is an ethoxylated cationic polyamine and is characterized in that R_4 is a substituted C3-C6 alkyl, hydroxyalkyl or aryl group; A1 is



and p is from 3 to 6.

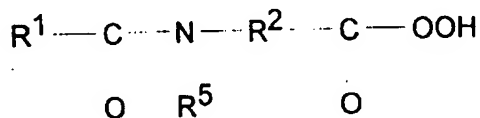
11. A granular detergent composition or component thereof according to any of Claims 6 to 8 wherein m is 0 and n is at least 20.
12. A granular detergent composition or component thereof according to any of Claims 1 to 11 wherein a cationic clay-soil removal/ anti-redeposition polymer is present characterised in that it has a backbone, at least 2M groups and at least one L-X group, wherein M is a cationic group attached to or integral with the backbone and contains an N^+ positively charged centre; and L connects groups M and X or connects group X to the polymer backbone; X is a nonionic group selected from the group consisting of H, C_1 - C_4 alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof; and L is a hydrophilic chain which contains the polyoxyalkylene moiety - $[(R^6O)_m(CH_2CH_2O)_n]-$;

13. A granular detergent composition or component thereof according to Claim 12 wherein said cationic polymer is an ethoxylated cationic polymer which has a backbone, selected from the group consisting of the polyurethanes, the polyesters, the polyethers, the polyimides, the polyalkyleneimines and mixtures thereof.
14. A detergent composition or component thereof according to any of Claims 1 to 13 wherein said hydrophobic organic peroxyacid compound has at least 7 carbon atoms.
15. A detergent composition or component thereof according to any of Claims 1 or 14 wherein said hydrophobic organic peroxyacid bleaching system comprises a hydrogen peroxide source and a hydrophobic organic peroxyacid precursor.
16. A detergent composition according to Claim 15 wherein said hydrophobic organic peroxyacid precursor is present at a level of from 0.2% to 10% by weight of the detergent composition.
17. A detergent composition or component thereof according to either of Claims 15 or 16 wherein the organic peroxyacid precursor compound is an amide substituted alkyl peroxyacid precursor compound selected from the group consisting of

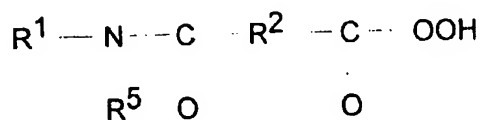


wherein L can be essentially any leaving group, R^1 is an aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms such that R^1 and R^5 in total not contain more than 18 carbon.

18. A detergent composition or component thereof according to any of Claims 1 or 13 wherein said hydrophobic organic peroxyacid bleaching system comprises a preformed organic peroxyacid.
19. A detergent composition according to Claim 18 wherein said preformed organic peroxyacid is present at a level of from 1% to 10% by weight of the detergent composition.
20. A detergent composition or component thereof according to either of Claims 18 or 19 wherein the preformed organic peroxyacid is selected from the group consisting of:



and



wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms such that R^1 and R^5 not contain more than 18 carbon atoms total.

21. A granular detergent composition or component thereof according to any of Claims 1 to 20, wherein a non-hydrophobic bleach precursor compound is present.
22. A granular detergent composition according to Claim 21 wherein the ratio of said non-hydrophobic bleach precursor compound to the water-soluble cationic compound is from 10:1 to 1:1.

23. A granular detergent composition according to Claim 21 or 22 wherein the non-hydrophobic bleach precursor compound is a N, N, N¹, N¹-tetra acetylated alkylene diamine.
24. A granular detergent composition according to any of Claims 1 to 23 wherein the composition is formulated in such a manner as to provide a wash pH of from 8.0 to 10.5.
25. A detergent composition according to any of Claims 1 to 24 wherein a heavy metal ion sequestrant is present at a level of from 0.1% to 10% by weight of the detergent composition.
26. A granular detergent composition or component thereof according to any of Claims 1 to 25 wherein a surfactant is present, selected from the group consisting of anionic, nonionic, cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.
27. A method of washing laundry in a domestic washing machine wherein an effective amount of a granular detergent composition according to any of Claims 1 to 26 is introduced into the drum of the washing machine, preferably before the commencement of the wash by use of a dispensing device which permits progressive release of said granular detergent composition into the wash liquor during the wash.

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/US97/16697

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : C11D 1/62, 3/395 US CL : 510/299, 309, 310, 375, 378, 443, 444, 504, 528 According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 510/299, 309, 310, 375, 378, 443, 444, 504, 528 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS ONLINE search terms: peracid precursor, bleach precursor, perborate, percarbonate				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	GB 2,268,879 A (LAPORTE ESD LIMITED) 26 January 1994, p. 1, lines 1-7; page 2, lines 9-11; page 2, line 16-page 3, line 18.	1-3		
A	EP 111,965 A2 (THE PROCTER & GAMBLE COMPANY) 27 June 1984.	1-3		
A	US 4,741,842 A (ADAMS) 03 May 1988.	1-3		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.				
<table border="0"> <tr> <td> * Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed </td> <td> *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *A* document member of the same patent family </td> </tr> </table>			* Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *A* document member of the same patent family
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Date of the actual completion of the international search 25 NOVEMBER 1997		Date of mailing of the international search report 12 JAN 1998		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer JOHN R. HARDEE <i>Regini Waller</i> Telephone No. (703) 308-0661		

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/16697

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-27
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-3

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

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